Universitat Rovira i Virgili
Escola Tècnica Superior d'Enginyeria Química
Departament d'Enginyeria Química

CATALYTIC WET AIR OXIDATION COUPLED WITH AN AEROBIC BIOLOGICAL TREATMENT TO DEAL WITH INDUSTRIAL WASTEWATER

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Memòria presentada per:
María Eugenia Suárez Ojeda

Per a optar al Grau de
Doctora en Enginyeria Química
Tesi dirigida per en Dr. Josep Font i en Dr. Julián Carrera

Membres del Tribunal de Tesi

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Juny 2006

El Dr. Josep Font, Professor Titular del Departament d'Enginyeria Química de la Universitat Rovira i Virgili de Tarragona i el Dr. Julián Carrera, Professor Agregat del Departament d'Enginyeria Química, de la Universitat Autònoma de Barcelona,

Fan constar que el present treball, amb el títol

CATALYTIC WET AIR OXIDATION COUPLED WITH AN AEROBIC TREATMENT TO DEAL WITH INDUSTRIAL WASTEWATER

que presenta la doctoranda na **MARÍA EUGENIA SUÁREZ OJEDA** per a optar al grau de Doctora en Enginyeria Química, ha estat dut a terme sota la nostra immediata direcció i que tots els resultats obtinguts són fruit del treball i l'anàlisi realitzats per l'esmentada doctoranda.

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

Tarragona, Juny de 2006

Dr. Josep Font	Dr. Julián Carrera
Professor Titular d'Enginyeria Química	Professor Agregat d'Enginyeria Química
Universitat Rovira i Virgili	Universitat Autònoma de Barcelona

Esta tesis está dedicada a Pedro, mi querido esposo:

Nuestro hogar está en cualquier parte del mundo, en el que los dos estemos juntos.

MariE

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ABREVIATTIONS, ACRONYMS AND SYMBOLS

WAO: Wet Air Oxidation

CWAO: Catalytic Wet Air Oxidation

LFS: Liquid Flowing Static

TOC: Total Organic Carbon

COD: Chemical Oxygen Demand

BOD: Biological Oxygen Demand

AOP: Advanced Oxidation Process

AC: Activated Carbon

LAS: Sodium Laurylbenzenesulfonate

BMP: Biochemical Methane Potential

WWTP: Wastewater Treatment Plant

DO: Dissolve Oxygen

OUR: Oxygen Uptake Rate

ATP: Adenosin Trifosfate

Y_H: Heterotrophic Growth Yield

PS: Peak Slope

PHe: Peak Height

S_{OE}: Oxygen Concentration in Equilibrium

S_{Ofin}: Oxygen Concentration in Equilibrium at maxim OUR

PA: Peak Area

HPV: High Production Volume

OECD: Organisation for Economic Co-operation and Development

USA: United States of America

EPA: Environmental Protection Agency of USA

PPL: Priority Pollutants List

EU: European Union

CERCLA: Comprehensive Environmental Response, Compensation, and Liability Act

RTECS: Registry of Toxic Effects of Chemical Substances

ATSDR: Agency for Toxic Substances and Disease Registry of USA

TGA: ThermoGravimetric Analysis

TWL: Total Weight Loss

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SUMARIO EN ESPAÑOL

OXIDACIÓN HÚMEDA CATALÍTICA CON AIRE ACOPLADA A UN TRATAMIENTO BIOLÓGICO AERÓBICO PARA TRATAR EFLUENTES INDUSTRIALES

La creciente rigidez de la legislación medioambiental actual, hace necesario el diseño de procesos eficaces para el tratamiento de aguas residuales industriales. Estos procesos deben garantizar que el agua tratada sea de fácil reutilización o bien, que pueda ser adecuadamente vertida al medioambiente sin que esto cause efectos adversos.

En este sentido, este estudio busca aplicar la oxidación húmeda con aire sin y con carbón activo comercial como catalizador ("Wet Air Oxidation"-WAO- y "Catalytic Wet Air Oxidation"-CWAO-), como técnica de pretratamiento de efluentes industriales con una alta carga de compuestos bio-recalcitrantes (por encima de 8 g l^{-1} en demanda química de oxígeno-DQO-). La idea es acoplar los efluentes industriales pretratados como parte integral de la entrada a un tratamiento biológico convencional. Los compuestos modelo seleccionados para este estudio fueron: fenol, o-cresol, 2-clorofenol, dodecilbenceno sulfato de sodio (DBS), anilina, p-nitrofenol, nitrobenceno y sulfolano.

Los experimentos de WAO fueron realizados en sistemas discontinuos y con tiempos de reacción de 30, 60, 90 y 120 minutos. Las temperaturas utilizadas en los experimentos WAO fueron 215, 240 y 265ºC manteniendo la presión parcial de oxígeno (P_{O2}) en 2 bar. En el caso del DBS, los experimentos de WAO fuero realizados con temperaturas de 180, 200 y 220ºC y 15 bar de P_{O2}.

Los ensayos de CWAO fueron realizados en continuo con un reactor de lecho fijo de goteo por un tiempo total de 72 h. El caudal de aire fue ajustado para garantizar oxígeno en exceso, mientras que el caudal de líquido fue fijado con el peso de lecho catalítico para proporcionar un tiempo espacial del líquido de 7.3 min. La P_{O2} fue ajustada a 2 bar mientras que la temperatura se fijó en 140 ó 160ºC.

Para establecer la influencia que tienen la temperatura y presión parcial de oxígeno sobre la reacción de oxidación de los compuestos seleccionados, los efluentes pretratados se caracterizaron mediante cromatografía líquida de alto rendimiento (HPLC), DQO, carbono orgánico total (COT) y aumento de la biodegradabilidad. En el caso de las pruebas en donde se utilizó carbón activo como catalizador, este también fue caracterizado antes y después de cada prueba en términos de los cambios sufridos por el catalizador en cuanto al peso y a las propiedades de superficie.

La biodegradabilidad de los efluentes procedentes de los distintos ensayos de oxidación fue determinada mediante pruebas respirométricas. En ellas se utilizó un respirómetro tipo LFS en el cual se monitoriza el oxígeno disuelto en la fase líquida (S_O). Al añadir un pulso de substrato, los microorganismos consumen el S_O a medida que metabolizan el sustrato. Posteriormente, se resuelve el balance de materia de oxígeno en la fase líquida y se obtiene la Tasa Máxima de Consumo de Oxígeno (OUR) y el Oxígeno Consumido (OC), que son indicadores de la biodegradabilidad, toxicidad o inhibición del substrato que se estudia. Para realizar las pruebas respirométricas de cada uno de los efluentes obtenidos de los tratamientos de oxidación, se empleó un pulso de sustrato de 20 mg DQO l^{-1}, se fijó una temperatura de 30+0.5ºC usando un baño termoestático y se inoculó el respirómetro con biomasa procedente de la EDAR del Puerto de Tarragona la cual tenía una concentración en sólidos volátiles de 2100+320 mg l^{-1}. El pH fue en todo momento de 7.5+0.5.

El objetivo global de este estudio fue hallar las condiciones apropiadas en la etapa de oxidación, en términos de: a) destrucción del compuesto modelo, b) preservación del catalizador en el caso de la oxidación húmeda catalítica con aire, c) distribución de intermedios y d) aumento de la biodegradabilidad, que permitiesen acondicionar los efluentes industriales fenólicos para su posterior depuración en una EDAR (estación depuradora de aguas residuales) convencional como parte integral de la entrada a la misma.

Cabe destacar, que cuando se utiliza carbón activo como catalizador en la CWAO varias reacciones y/o fenómenos ocurren en paralelo. No solo existe la reacción de oxidación del compuesto modelo y de sus intermedios de reacción, sino también la oxidación/combustión de la matriz carbonosa y las reacciones de acoplamiento oxidativo (adsorción irreversible) que ocurren sobre la superficie del carbón activo. Simultáneamente, también está ocurriendo la absorción del compuesto modelo y de sus intermedios de reacción. Las reacciones paralelas y la absorción de los compuestos no pueden ser estudiadas separadamente sin afectar el desempeño global del sistema de oxidación, es por esta razón que solo puede extraerse información global de la caracterización del efluente y del catalizador e intentar relacionarla con el aumento obtenido en la biodegradabilidad.

Las conclusiones más importantes derivadas de este estudio son:

- De la primera etapa del estudio en la cual se estableció la factibilidad del tratamiento de los compuestos modelo por CWAO a 140ºC y 2 bar de P_{O2}, se demostró que el carbón activo se comporta como catalizador y absorbente y que además es suficientemente activo como para promover la oxidación de fenol, o-cresol, 2-clorofenol y DBS, con conversiones de entre el 33 y el 55%, en las condiciones estudiadas. Por el contrario, el resto de compuestos (anilina, p-nitrofenol, nitrobenceno y sulfolano) no pudieron ser destruidos en una extensión aceptable, obteniéndose conversiones por debajo del 8%.

- La destrucción del compuesto modelo (conversión, reducción de la DQO y del COT), la distribución de los intermedios de reacción y el aumento de la biodegradabilidad demostraron ser muy sensibles al aumento de la temperatura pero no significativamente al cambio en la P_{O2}. Sin embargo, la preservación del carbón activo se vio muy afectada tanto por la temperatura como por la P_{O2} utilizadas en los experimentos. Debe notarse que el carbón activo también sufre una oxidación que modifica sus propiedades superficiales y que causa un apreciable consumo del mismo.

- La reactividad de los compuestos modelo presentó un comportamiento dependiente de las condiciones de operación empleadas y del comportamiento del catalizador. Así, dos mecanismos de reacción diferentes, sustitución aromática nucleofílica o electrofílica, pueden servir para explicar los distintos niveles de reactividad observados. De cualquier manera, la conversión alcanzada y por ende la reactividad observada para cada compuesto puede verse afectada tanto por la cinética de la reacción como por el comportamiento del catalizador, por lo que las evidencias observadas para definir el mecanismo de reacción pueden no ser suficientes. Sin embargo, los mecanismos propuestos están basados en la generación de especies reactivas provenientes del oxígeno (radicales y aniones), por lo que el carbón activo puede considerarse un promotor en la generación de este tipo de especies que a su vez presentan un comportamiento como nucleófilos y como electrófilos.

- Se demostró que la respirometría LFS es una técnica versátil y confiable para determinar el efecto de cada uno de los intermedios de oxidación sobre el fango activado y que además puede ayudar a decidir los criterios que permitan el acoplamiento entre ambos tratamientos.

- Los resultados obtenidos de las respirometrías permitieron clasificar los intermedios de reacción mayoritarios como rápidamente biodegradables, inertes y tóxicos y/o inhibitorios. Para la caracterización, se utilizaron fangos no adaptados procedentes de una EDAR urbana.
- De los ácidos carboxílicos, los rápidamente biodegradables fueron los ácidos fumárico, propiónico, acético, succínico, fórmico y glioxílico, mientras que los ácidos, oxálico, maleico, malónico, 4-hidroxibenzoico y ácido salicílico (2-hidroxibenzoico) se comportaron como compuestos inertes. Los intermedios de reacción tipo quinona se comportaron como compuestos inertes a 1 mg DQO l^{-1}, pero como intermedios inhibitorios (catechol) o tóxicos (hidroquinona y p-benzoquinona) a 4 mg DQO l^{-1}. El fenol, o-cresol, 2-clorofenol y DBS se clasificaron como compuestos inertes aún cuando a 8 mg DQO l^{-1}, el o-cresol presentó un comportamiento inhibitorio.
- La biodegradabilidad de los efluentes pretratados provenientes de la oxidación húmeda con aire puede ser predicha conociendo su composición, la concentración y las propiedades de biodegradación de cada intermedio de reacción.
- La mejor condición para el pretramiento de fenol, o-cresol y 2-clorofenol con CWAO resultó ser de 160ºC y 2 bar de P_{O2}. A estas condiciones, la destrucción de la DQO fue la máxima para el fenol y el 2-clorofenol y la segunda más alta para el o-cresol. Adicionalmente, la preservación del catalizador es claramente más elevada a 2 bar que a 9 bar de P_{O2}. Finalmente, la proporción de DQO rápidamente biodegradable obtenida a estas condiciones en los efluentes pretratados fue prácticamente la máxima para los tres compuestos.
- Los efluentes pretratados se acoplaron, posteriormente, a una planta piloto biológica de fangos activados. Se demostró que el tratamiento integrado CWAO-biológico de o-cresol y fenol es efectivo alcanzando reducciones en la DQO de hasta el 90% sin causar ningún efecto adverso sobre la biomasa y utilizando proporciones de hasta el 30% de los efluentes pretratados por CWAO en la entrada a la EDAR piloto. Por lo tanto, la CWAO acoplada a un posterior tratamiento biológico resultó ser un tratamiento efectivo, en términos de rendimiento, operación y legislación, para aguas residuales industriales con un alto contenido de compuestos fenólicos.

- Sin embargo, para el tratamiento de fenol y o-cresol por medio de WAO, los intermedios de reacción rápidamente biodegradables aparecieron en una proporción menor, mientras que los posibles tóxicos/inhibidores se produjeron en una proporción mayor que en el tratamiento con CWAO, por lo que pudo demostrarse que la CWAO presenta un mayor aumento de la biodegradabilidad que la WAO.
- Por el contrario, el 2-clorofenol puede ser efectivamente tratado tanto por CWAO como por WAO, por lo que la selección del pretramiento ha de estar basada en la factibilidad técnico-económica o en la disponibilidad de pretratamiento de un tipo u otro.
- Finalmente, el DBS también puede ser destruido efectivamente tanto por WAO como CWAO al igual que el 2-clorofenol. Sin embargo el uso de una P_{O2} de 9 bar en CWAO causó el desarrollo un sistema espumante que no fluía adecuadamente por el lecho catalítico. A su vez, ello se tradujo en un pobre comportamiento de la oxidación en el reactor de CWAO. Sin embargo, cabe destacar que el aumento de la biodegradabilidad del DBS pretratado con CWAO es muy superior al que se obtuvo con el resto de compuestos fenólicos.

Los resultados obtenidos muestran una prometedora vía para el desarrollo de procesos químico-biológico acoplados para el tratamiento eficiente de aguas residuales con un alto contenido de compuestos tóxicos o no biodegradables, lo cual permitiría instalar plantas de oxidación para tratar efluentes específicos de producción industrial que podrían, más tarde, ser integrados en la gestión conjunta de depuración biológica de aguas.

CHAPTER I. INTRODUCTION AND MOTIVATION

Outlook

Clean fresh water is essential to life. Unfortunately, since the Industrial Revolution, most of Europe's rivers have been treated more like a convenient way of transporting waste to the sea, destroying the biodiversity of thousands of kilometres of waterways, harming human health, and polluting coastal waters in the process.

The past decades have seen significant progress in treating the sewage and industrial wastes which are being pumped into Europe's river systems, resulting in lower levels of most pollutants and a measurable improvement in water quality. Not only the quality of water but also the quantity available for human use is of importance and more and more frequently, there are problems with water scarcity around large cities and in southern Europe. Therefore, the wastewater treatment and recovery is mandatory nowadays.

This chapter aims to describe very briefly the problems with fresh water availability, the water pollution timeline and legislation, passing throughout the industrial effluents problem and ending with the ways to solve this specific problem. Also a succinct description of the model compounds of industrial wastewater selected in this study is performed.

I.1. Water Scarcity problem

Fresh and unfrozen water constitutes only 0.65% of the water on Earth, which is mostly groundwater (0.62%). Only 0.03% is surface water in lakes, rivers, soil and the atmosphere [1]. From the total hydrosphere, as can be seen in Figure I.1, only 2.5% is fresh water (the most economical source of water) suitable for drinking, growing crops and industrial uses and 99% cannot be tapped easily with a foreseeable technology [2], because it is in form of glaciers, permanet snows and groundwater.

In calculating how much fresh water is available for human use, what accounts for is not the total sum of global fresh water supplies or water use, which vary for each country and cannot be grupped in a single global statistics, but the rate at which fresh water resources are renewed or replenished by the global hydrologic cycle. Powered by the sun, this cycle each year deposits about 113000 cubic kilometers of water on the continents and islands as rain and snow. Of that, about 72000 cubic kilometers evaporates back into the atmosphere, leaving only 41000 cubic kilometers per year to replenish aquifers or to return by river or other runoff to the oceans [2]. If all the world's water fits into a bathtub, the portion of it that could be used sustainably in any given year would barely fill a teaspoon [3].

Moreover, not all of this 41000 cubic kilometers can be captured for human use. More than the half flows unused to the sea in floodwaters and as much as the eighth falls in areas too far from human habitation to be recovered for use. Some water experts suggest the practical upper limit of the world's available renewable fresh water lies between 9000 and 14000 cubic kilometers per year [4, 5]. And a substantial proportion of this amount is needed to sustain natural ecosystems in and around rivers, wetlands and coastal waters and the millions of living species they contain.

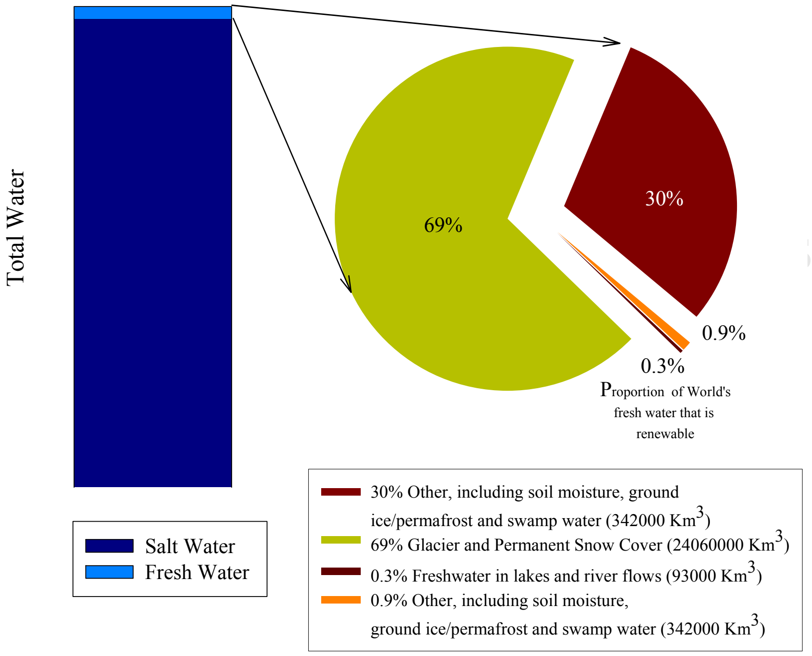

Figure I.1. Fresh water distribution [2]

On the other hand, the Earth was home to 6 billion people in 2002: 1.1 billion of them lacked safe water and 2.6 billion lacked adequate sanitation [6]. As a consequence, water and sanitation-related diseases are widespread. Nearly 250 million cases are reported each year, with more than 3 million deaths annually or about 10000 a day. Diarrhea diseases impact children most severely, killing more than 2 million young children per year in the developing world (Figure I.2).

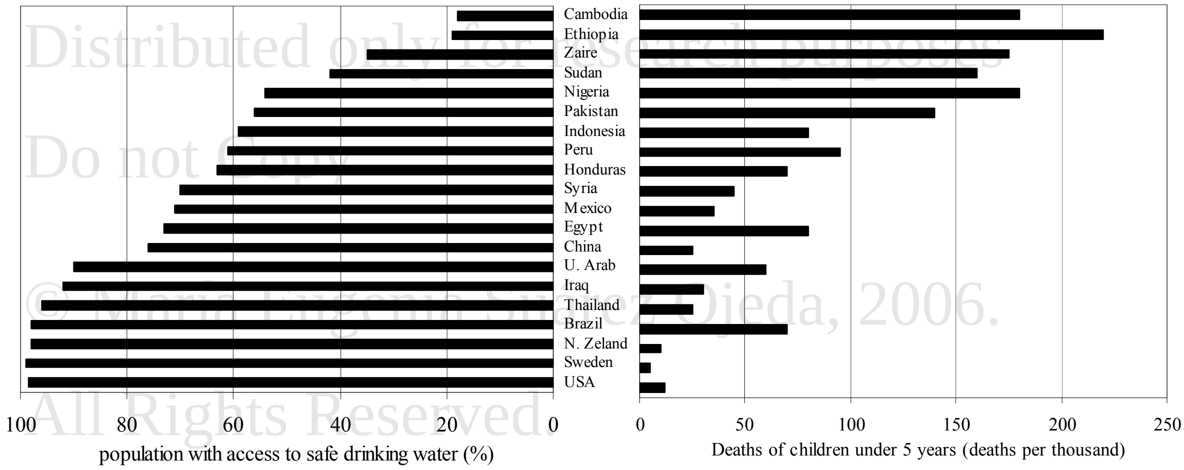

Figure I.2. Access to safe water resources and deaths of children [7]

In spite of hard work and laudable progress, the number of people without access to both water supply and to sanitation in developing countries remained practically the same throughout the 90s. The increase in served population was just enough to keep pace with population growth. According to the Global Water Supply and Sanitation Assessment 2000 Report [8], the majority of the world's population without access to improved water supply or sanitation services lives in Africa and Asia. Two-thirds of people without access to improved water supply and more than three-quarters of those without access to improved sanitation live in Asia (Table I.1).

Table I.1. Water supply and sanitation in 1980 and 1994 [9]

	Millions without safe water supply		Millions without adequate sanitation	
Region	1980	1994	1980	1994
Africa	243	381	315	464
Latin-American and the Caribbean	109	97	150	176
Asia and the Pacific	1461	627	1250	2206
Western Asia	12	10	20	26
Total	1827	1115	1740	2873

Even given the more encouraging population projections from the 1996 UN data [10], the problem of water scarcity will still get worse before any further improvement. As Figure I.3 indicates, Popular Action International [11] estimates that by the year 2050, according to the UN 1996 medium projection, the percentage of the world's population in countries experiencing water stress and scarcity will increase more than fivefold[i].

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[i] This water availability figure do not include supplies of ground water or desalinisation plants, also this figure take no account of the timing or seasonality of this availability.

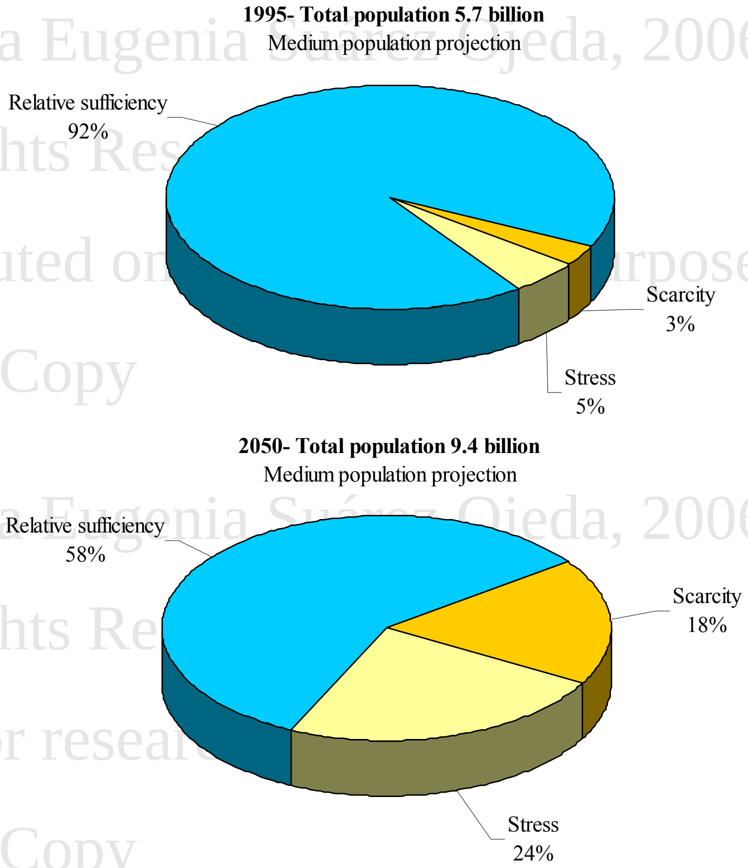


Figure I.3. World population suffering freshwater scarcity, stress and relative sufficiency in 1995 and 2050.

In Europe, the situation is far from better, substantial changes in precipitation patterns, possibly linked to climate change, are already apparent in Europe. In some northern countries there has been a marked increase in precipitation in recent decades, particularly in winter, while declining rainfall is a recent feature of southern and central Europe, especially in summer. These trends are expected to continue, causing serious water stress in parts of southern Europe in particular. In parts of the north, additional rainfall will increase river flow. Water availability may increase by 10 % or more in much of Scandinavia and parts of the United Kingdom. In southern Europe a combination of reduced rainfall and increased evaporation will cause a reduction of 10 % or more in the run-off in many river basins in Greece, southern Italy and Spain, and parts of Turkey (Figure I.4).

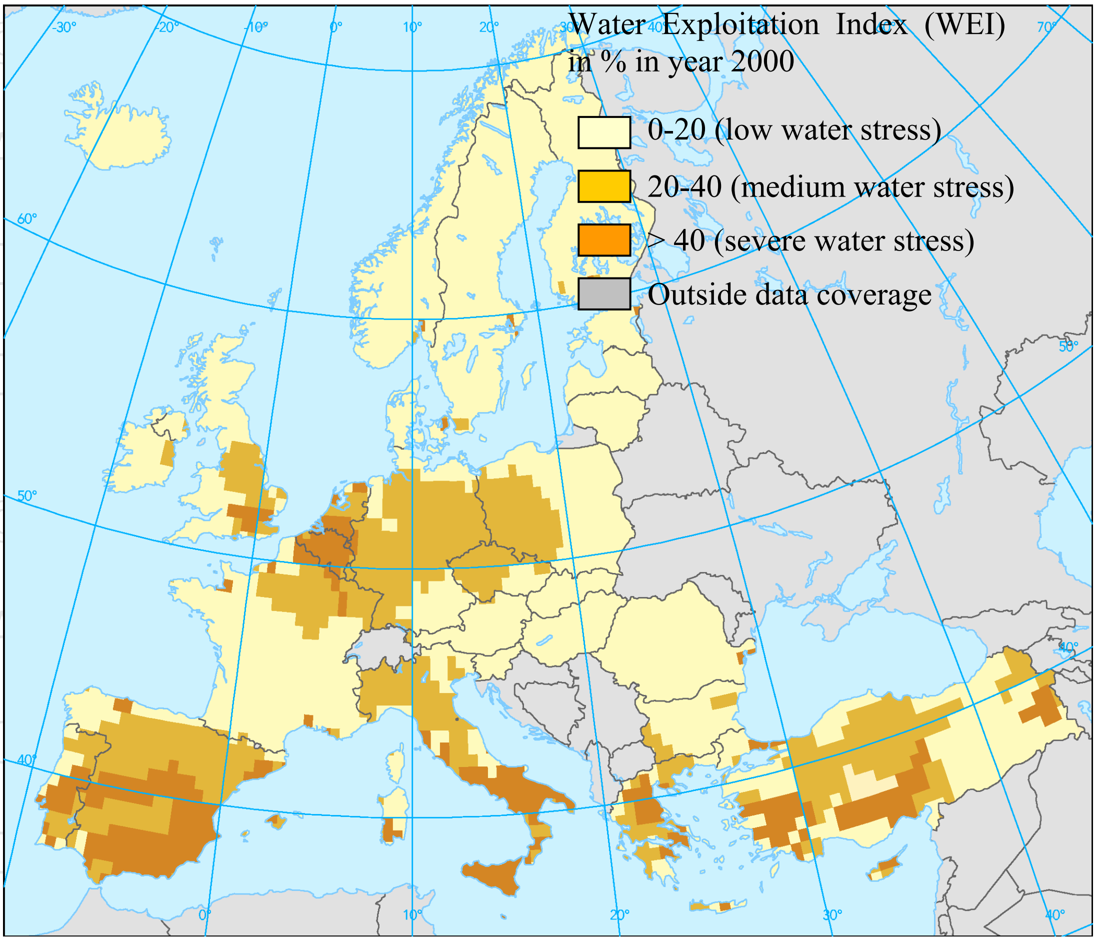


Figure I.4. Water stress in 2000 [12].The water exploitation index (WEI) is the mean annual total abstraction of freshwater divided by the mean annual total renewable freshwater resource at the country level, expressed in percentage terms.

In southern Europe, this reduced supply will be made worse by sharply rising demand, particularly from farmers needing more water to irrigate their crops. Water stress in many river basins in this part of Europe can be expected to increase (Figure I.5). Prominent examples will include the Guadalquivir and Guadiana rivers in Spain (and the latter also in Portugal) and the Kizil Irmak in Turkey. The Guadalquivir is expected to see more than 90 % of its flow abstracted by 2030. Spain is already responding to future anticipated shortages with plans for a large network of desalination works in the country and a push to more efficient irrigation systems. The drought conditions already apparent on the Iberian Peninsula in spring/summer 2005 underline the urgency of such measures. Where rivers cross national boundaries the demands of shared extraction add to the complex situation, for example in 2005 the flow of some rivers into Portugal were highly reduced, impacting the generation of hydropower, water available for irrigation and even water for human consumption.

In general, northern Europe is likely to become more flood prone and southern Europe more drought prone as the extra energy in the climate system increases the probability of extremes not just droughts but also severe storms and floods, such as those in central Europe in recent years.

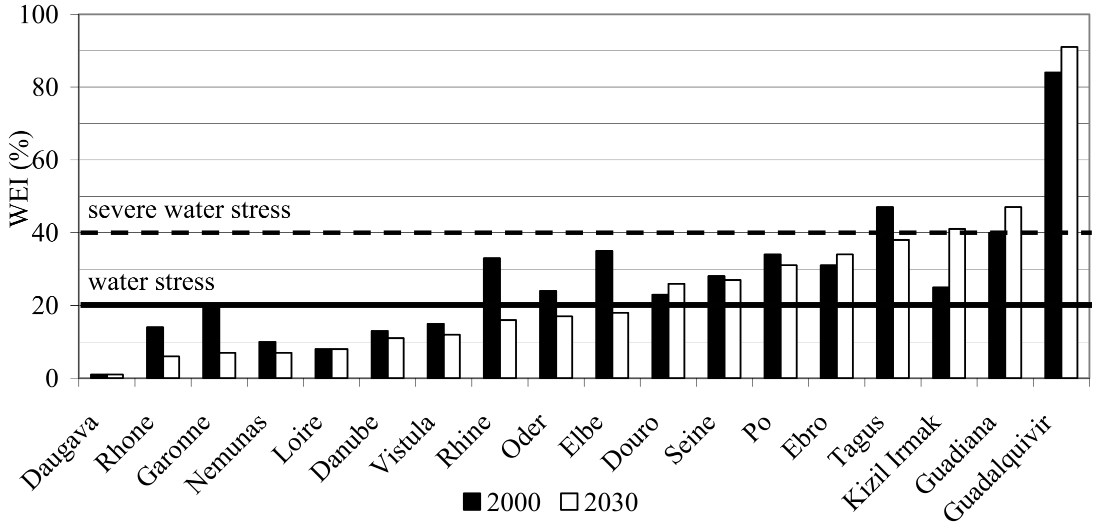


Figure I.5. Water stress in large European river basins, 2000 and 2030 [12]

I.2. Water Pollution Management and regulations.

In our consumer-based economy, Chemistry plays an essential role in our attempt to feed world's population, to find new sources of energy, to maintain the humankind, to improve health and to eliminate sickness, to provide substitutes for rare raw materials, to design necessary materials for new information and communication technologies and to monitor and protect our environment. In that way, over 14 million different molecular compounds have been synthesised during the last century and about 100000 can be found in the market. Only a small fraction of them are found in the Nature [13]. This increasing design of new materials has produced new sources of pollution which have often turned to be toxic, persistent and difficult to eliminate from the aquatic systems.

A critical issue associated to this rapid industrial and technological development is the sustainable wastewater management. The environmental concern is nowadays expressed by more and more stringent governmental regulations imposing lower pollutant discharge limits. So, for many industrial sectors, pollution prevention, waste minimisation and reuse are being increasingly integrated in their environmental policies. Thus, the challenges faced by chemical and related industries are to design efficient and cheap remediation processes and minimisation strategies for the water pollution problems.

I.2.1 Wastewater treatment timeline: The 20th century.

The Twentieth century witnessed a revolution in waste management, environmental science and societal views toward pollution. Scientific discovery, debates on social priorities, and government awakening evolved through a century beginning with unhindered pollution and ending with attempts at total control [14]. As Table I.2 shows, the environmental management has evolve from little pollution control in 1900, passing through the post WWII period, which might be considered a turning point, to the 1970s/1980s periods when technology and regulations coalesced into comprehensive control objectives. The century ended with continued learning about how to meet such objectives. Moreover, our ability to understand the pollution problem is related to the advances on analytical chemistry, and because of that the regulatory framework we know today for pollution did not exist before the 1970s (Table I.2).

Table I.2. Decades of progress in environmental management and legislation and in analytical chemistry [14].

Decade	Progress in environmental management	Evolution of Environmental analytical chemistry	Environmental legislation timeline in USA
1900	Essential unhindered waste disposal	1st "Standard Methods" publication, general parameters	Federal Rivers and Harbours Act (protect navigation from gross pollution)
1910	More waste (WWI industrialization and urban growth) but continued limited control	3rd edition of "Standard Methods", general parameters. Dissolved oxygen (S_O) and biological oxygen demand (BOD) methods improvement. Phenols detection > 100 mg l^{-1} (colorimetric methods)	State boards of Health established in all states. Public Health service established.
1920	Advent of water pollution science and the quantification of stream pollution	BOD methods improvements. Phenols detection > 10 mg l^{-1} (colorimetric methods)	Oil pollution act (oil spills in coastal waters)
1930	Evolution of engineering practices and state control	8th edition of "Standard Methods", general parameters. S_O, chemical oxygen demand (COD) and BOD methods improvement. Phenols detection > 10 mg l^{-1} (colorimetric methods). Petroleum hydrocarbon fractions (not compound specific)	Sewage construction grants
1940s	Level of regulatory control debated extensively, but WWII hiatus	Infrared (IR) methods for some organics > 500 mg l^{-1}. Benzene > 100 mg l^{-1}. DO by mercury electrode. Ultra visible (UV) photometry for some organics > 30 mg l^{-1}. Total petroleum (gravimetric)	Sewage construction grants; Federal water pollution control act.
1950	Post war industrial boom added pressure as federal and state regulation grew	Portable DO meter. Introduction to mass spectroscopy (MS) and atomic absorption spectroscopy (AAS). IR method advances. Column chromatography	Air pollution control act (focus on research); Federal water pollution control act.
1960	Birth of modern pollution legislation, Federal lead, states implemented	11th edition of "Standard Methods", added wet chemistry inorganics. Paper and gas chromatography (GC) advances. Fluorescence spectroscopy. IR method advances. Polychlorobiphenyl (PCB) and DDT research level analysis by GC. First commercial AAS	Federal water pollution control act amendments of 1961 (Extended federal enforcement authority to coastal and interstate waters; industrial pollution control remained with states). Clean air act (emission standards). Water quality act (water quality standards for all interstate waters). Solid waste disposal act. Clean water restoration act. Federal Air quality act (air quality criteria, state development of air quality standards, and air quality control regions).
1970	Coalescence of total environmental control, zero discharge as a goal	PCB Aroclor and separation refinement. First government methods for pesticides. GC refinements (cleanup, flame ionization, electron capture). MS and magnetic resonance (NMR) refinements. Inductive coupled plasma atomic emission spectrophotometer (ICP). First Environmental Protection Agency (EPA-USA) manuals on organics and trace metal analysis.	Clean air act amendments (air standards). National environmental policy act (environmental impact studies). Resource recovery act (hazardous waste practices, recycling and energy recovery). Executive order 11574 for EPA establishment and wastewater discharge limits. Federal water pollution control act amendments of 1972 (federal water law, treatment standards, toxic chemicals). Safe drinking water act (national drinking water standards). Resource conservation and recovery act (federal regulation for hazardous waste). Toxic substances control act (toxicity testing requirements for new chemicals commerce; PCB controls).
1980	Hazardous waste site frenzy, everyone in guilty	First EPA-USA manual on hazardous waste analysis	Comprehensive Environmental response, compensation and liability act (CERCLA). Hazardous and solid waste amendments (landfill controls)
1990	Regulatory refinement. Waste management is an integral part of doing business	20th edition of "Standard Methods", 350 separate measurements methods. Dioxin analysis > 1 part per quadrillion.	

The "how clean is clean" environmental quality issue reflects our growing understanding about environment and public health. Three types of standards evolved (discharge standard, ambient environmental standards and consumer standards). Environmental standards existing in 1900s were qualitative measure of gross effects (odour, floating materials or fish killing) whereas now, are related to ratio between biological oxygen demand and dissolved oxygen (BOD/DO) in streams, turbidity, oil/grease, phenols and nutrients.

Now, in the Twenty-first Century, the key issue remaining today is the same issue persisting throughout the Twentieth Century: how much environmental and pollution control is necessary and economically viable?

I.2.2 Wastewater regulations in Europe and in Spain.

Environmental action by the European Community as a whole began in 1972 with the adoption of more than 200 pieces of legislation, chiefly concerned with limiting pollution by introducing minimum standards, notably for waste management, water pollution and air pollution.

EU policy on waste management involves three complementary principles:

a) Eliminating waste at source and breaking the link between waste creation and growth, amongst other things by improving product design.

b) Encouraging waste recycling and re-use, for specific waste flows in particular.

c) Improving the method of final disposal, for example by reducing pollution caused by waste incineration and using landfill only as a last resort.

Since the adoption of the 1975 framework Directive on waste [15], legislative developments have been based on these three principles, while giving more and more weight to prevention and recycling, as borne out by the thematic strategy on that subject.

For a long time, Community legislation left waste treatment to the public authorities. The European Union has therefore defined the waste flows to be treated as a priority and has laid down rules *inter alia* on packaging waste , batteries and oils.

The legislation has since moved towards assigning more responsibility to the producer. For instance, the Directive of September 2000 on end-of-life vehicles [16] establishes a system for collecting such vehicles at the manufacturer's expense. Likewise, two Directives on waste from electrical and electronic equipment and restricting the use of certain dangerous substances in such equipment were adopted in 2002 [17, 18].

Reflecting the new environmental conscience, the European Union, in the Directive 2000/60/EC, [19] points out that "water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such". Also, the Urban Waste Water Treatment Directive (91/271/EEC) [20] aims to protect the environment from the adverse effects of urban wastewater discharges. It prescribes the level of treatment required before discharge and has to be fully implemented in the EU-15 by 2005 and in the EU-10 by 2008–2015. The directive requires Member States to provide all agglomerations of more than 2000 population equivalent with collecting systems and all wastewaters collected to be provided with appropriate treatment by 2005. Therefore, the direct disposal of domestic use and industrial activity wastewaters are impossible nowadays because causes a considerable impact in the environment. This fact, together with the necessity of recycling this water for new uses, makes practically essential the purification of wastewater to achieve the desired quality degree.

In the EU, over the last twenty years, marked changes have occurred in the proportion of the population connected to wastewater treatment as well as in the wastewater treatment technology involved. In northern countries most of the population are today connected to wastewater treatment plants with tertiary treatment, which efficiently removes nutrients (nitrogen or phosphorus or both) and organic matter from the wastewater. As shown by Figure I.6, in the central Europe countries more than half of the wastewater is treated by tertiary treatment. Southern countries and the Accession countries only have around half of the population connected to wastewater treatment plants at the moment. 30 to 40 % of the population are connected to secondary or tertiary treatment. These changes have resulted in improvement of the state of water bodies with a decrease in concentration of orthophosphates, total ammonium and organic matter over the past ten years. In the EU these decreases are linked with the implementation of Directive 91/271/EEC. In the Accession Countries decreases are due to the general increase in the level and extent of wastewater treatment and because of the recession associated with the transition to market-oriented economies [12].

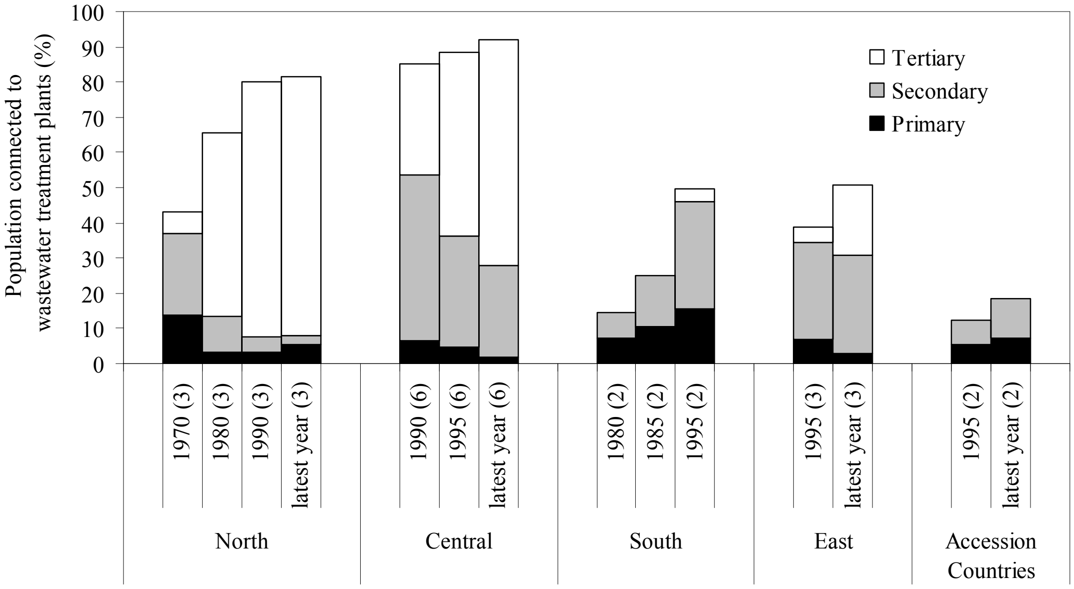


Figure I.6. Percentage of each treatment type as defined by the Urban Waste Water Treatment Directive (91/271/EEC) by region: Nordic: Norway, Sweden, Finland; Central: Austria, Denmark, England and Wales, the Netherlands, Germany, Switzerland; Southern: Greece, Spain; East: Estonia, Hungary and Poland; Accession Countries: Bulgaria and Turkey.

Finally, the Directive 2000/60/EC and also the Spanish Water Act 1/2001 (article 93) [21] defines the pollution as the "direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment".

According to that, a pollutant can be classified as physical, chemical or biological pollutant:

a) Physical pollutants: Substances giving colour, odour, solids or water streams with high temperatures.

b) Chemical pollutants: They are classified into organic (domestic wastes, agricultural wastes and industrial wastes) and inorganic (metallic salts, heavy metals and dissolved gases).

c) Biological pollutants: Microorganisms that can be pathogenic organisms and therefore can cause several diseases.

The European Union made a list of dangerous compounds (Directive 2000/60/EC, Annex VIII: Indicative list of the main pollutants), considered as contaminants. The aim of this Directive is to achieve the progressive reduction of emissions of hazardous substances to water. The list of the updated priority pollutants has been presented in the Decision 2001/2455/EC [22].

I.3. The Industrial effluents problem

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 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 [23].

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 [24].

The importance of phenolic effluents, besides 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. Table I.3 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 [25].

Table I.3. Phenolic compounds European emissions to water (2001) [25].

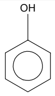
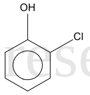
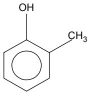
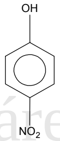
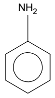
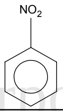
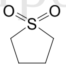
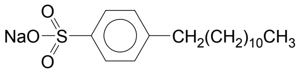
Country	Direct emissions		Indirect emissions	
	Total (kg/year)	% of European emissions	Total (kg/year)	% of European emissions
Denmark	89	0.02	3800	0.40
Finland	131	0.04	-	-
Portugal	784	0.21	80350	8.39
Sweden	1030	0.28	-	-
Austria	1370	0.37	228020	23.80
Greece	2020	0.55	-	-
Belgium	2500	0.68	3180	0.33
Netherlands	3380	0.91	1270	0.13
Germany	13010	3.52	448360	46.80
Spain	24020	6.50	3860	0.40
Italy	38520	10.42	8763	9.15
France	47600	12.87	34130	3.56
United Kingdom	231010	62.49	67140	7.01
Total	365464	100.00	878873	100.00

I.4. Model Compounds Selected for this Study

I.4.1 Description and eligibility criteria

Recognised toxic compounds like phenol, o-cresol, 2-chlorophenol, p-nitrophenol, nitrobenzene, aniline, sulfolane and an anionic surfactant named sodium dodecylbenzenesulfonate (DBS) were chosen for this study as model compounds of industrial effluents. 2-chlorophenol, o-cresol and DBS are model compounds from the families of cresols, chlorophenols and sodium salts of linear alkylbenzene sulfonates (LAS), respectively. Some of the characteristics of the model compounds can be found in Table I.4.

Table I.4. Model compounds studied in this work.

Compounds*	Molecular Formula	Molecular Structure	Boiling Point (ºC)	Solubility (g l^{-1} water) at 20ºC
Phenol	C_6H_6O		182	47
2-Chlorophenol	C_6H_5ClO		176	285
o-Cresol	C_7H_8O		191	25
p-Nitrophenol	$C_6H_5NO_3$		279	12
Aniline	$C_6H_5NH_2$		184	34
Nitrobenzene	$C_6H_5NO_2$		211	1.9
Sulfolane	$C_4H_8O_2S$		287	miscible
DBS	$C_{18}H_{29}NaO_3S$		>300	soluble

* Purchased to Aldrich at 99% purity, DBS purchased at technical grade.

The selection of the model compounds was based on the following factors (Table I.5):

a) It is a High Production Volume Chemical (HPV) according to the Organisation for Economic Cooperation and Development (OECD) (production > 1000 ton per year)

b) It is in the Environmental Protection Agency (EPA) Priority Pollutants List (PPL), in the European Union (EU) Directive 2000/60/EC or in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Priority List of Hazardous Substances.

c) It is a recognised (or at least suspicious) toxic by the International Chemical Safety Cards, the Registry of Toxic Effects of Chemical Substances (RTECS) and the toxicological profiles made by the Agency for Toxic Substances and Disease Registry (ATSDR) in USA.

In the case of DSB, it is known that is biodegradable, but its remediation by biological means is still difficult, since as much as 30-35% of the DSB can be adsorbed and left untreated in the sludge in biological reactors [26].

Table I.5. Factors that influence the selection of model compounds

Compounds	Included in EPA PPL list?	Included in EU Directive 2000/60/EC?*	Ranking in CERCLA List (total listed : 275)	RTECS Information
Phenol	Yes	Yes	162	Toxic for aquatic organisms Tumorigen Mutagen Reproductive Effector Primary Irritant
2-Chlorophenol	Yes	Yes	247	Toxic to aquatic organisms May cause long-term effects in the aquatic environment Tumorigen Mutagen Reproductive Effector
O-Cresol	No	Yes	194	Toxic to aquatic organisms Tumorigen Mutagen Primary Irritant
p-Nitrophenol	Yes	Yes	256	Toxic to aquatic organisms Causes methaemoglobinaemia Primary Irritant
Aniline	Yes	Yes	Not listed	Carcinogenic Causes methaemoglobinaemia Reproductive Effector
Nitrobenzene	Yes	Yes	Not listed	Carcinogenic Causes methaemoglobinaemia
Sulfolane	No	Yes	Not listed	Moderate Irritant
DBS	No	Yes	Not listed	Toxic to aquatic organisms Primary Irritant

*The model compounds could be included in the Annex VIII of the Directive 2000/60/EC but are not listed as priority pollutants in the decision 2001/2455/EU. However, phenol is a priority substance (EC 1179/94, OJ L131, 26.5.94, p.3.) under Regulation 793/93.

I.4.2 Uses and Related Industries

Phenol is a monosubstituted aromatic hydrocarbon. In its pure state, it exists as a colourless or white solid. Phenol gives off a sweet, acrid smell detectable to most people at 40 ppb in air, and at about 1 to 8 mg l^{-1} in water [27].

The largest use of phenol is as an intermediate in the production of phenolic resins, which are used in the plywood, adhesive, construction, automotive, and appliance industries. Phenol is also used in the production of synthetic fibbers, such as nylon, and for epoxy resin precursors such as bisphenol-A. Phenol is toxic to bacteria and fungi, and is also used as disinfectant. Because of its anaesthetic effects, phenol is used in medicines such as ointments, ear and nose drops, cold sore lotions, throat lozenges, and antiseptic lotions. The industries that use phenol are listed in Table I.6 [28].

Table I.6. Uses of phenol in the industry.

Industrial sector	Uses
Primary Metals	blast furnaces and steel mills, non-ferrous wire drawing and insulating, grey and ductile iron foundries, malleable iron foundries, motor vehicle parts and accessories, and aluminium foundries
Stone, Clay and Glass Product Manufacture	mineral wool, abrasive products, asbestos products, products of purchased glass, non-clay refractories, minerals (ground or treated), cement - hydraulic, lime manufacture
Rubber and Plastic Parts Manufacture	laminated plastics plate & sheet, custom compound purchased resins, tires and inner tubes, unsupported plastics film & sheet
Petroleum Products	petroleum refining, petroleum and coal products, lubricating oils and greases. Transportation Equipment Manufacture - motor vehicle parts and accessories, railroad and aircraft equipment
Wood Products Manufacture	reconstituted wood products, softwood veneer and plywood, hardwood veneer and plywood, structural wood members, sawmills & planing mills
Textile Mills	tire cord and fabrics, coated fabrics (not rubberised), broad woven fabric mills (wool and cotton)
Electronic Equipment Manufacture	engine electrical equipment, commercial lighting fixtures, transformers, electric house wares and fans, non-current-carrying wiring devices, semiconductors and related devices, printed circuit boards, switchgear and switchboard, relays and industrial controls
Industrial Machinery Manufacture	paper industries machinery, machine tools (metal cutting types)

The consumer products that may contain phenol are agricultural chemicals, disinfectants (non-agricultural), general antibacterials and antiseptics, household hard surface cleaners (liquid), lubricating oils, automotive chemicals, paint and varnish removers, pharmaceutical preparations, synthetic resins and rubber adhesives and wood office work surfaces (modular systems).

The family of cresols are conformed by the isomers ortho-cresol (o-cresol), meta-cresol (m-cresol), and para-cresol (p-cresol). Pure cresols are colourless chemicals, but they may be found in brown mixtures such as creosote and cresylic acids (e.g., wood preservatives). Because these three types of cresols are manufactured separately and as mixtures, they can be found both separately and together. Cresols can be either solid or liquid, depending on how pure they are; pure cresols are solid, while mixtures tend to be liquid. Cresols have a medicinal smell (odour) and when dissolved in water, they give it a medicinal smell and taste.

Cresols do not evaporate quickly from water, but in rivers and lakes, they can be removed by bacteria. Dissolved cresols can pass through soil into underground water sources. This may be a problem at hazardous waste sites where cresols are buried. Once cresols are in the water table, they may stay there for months without changing. Cresols in air quickly change and break down into smaller chemicals, some of which irritate the eyes.

Cresols are natural products that are present in many foods and in animal and human urine. They are also present in wood and tobacco smoke, crude oil, and coal tar. In addition, cresols also are man-made and used as disinfectants and deodorisers, to dissolve substances, and as starting chemicals for making other chemicals.

In the case of o-cresol, approximately [29] 60% of this compound is derived from coal tar and crude oil by using classical techniques such as distillation, stripping or liquid-liquid extraction. About 40% is obtained synthetically by alkylation of phenol with methanol, either in the vapour or liquid phase. Alkaline hydrolysis of chlorotoluene mixtures, and occasionally o-chlorotoluene have also been used as a production route of o-cresol, is also a by-product in the synthesis of 2,6-xylenol .

In 90% of the uses, cresols are organic intermediates in manufacturing of phenolic and epoxy resins and plasticisers (phosphate esters), herbicides, rubber and plastic antioxidants, dyes, deodorising and odour-enhancing compounds, fragrances and pharmaceuticals. Additional industrial uses of o-cresol or mixtures of cresols are antiseptics and disinfectants, cleaning compounds, degreasers, automotive cleaners, solvent, paint strippers and paints, adhesive and connected products, sealing adhesive masses, additive to phenol-formaldehyde resins, fibber treatment, wood preservatives, photography, ore flotation agent and cutting oils.

Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. There are five basic types of chlorophenols: mono-chlorophenols, di-chlorophenols, tri-chlorophenols, tetra-chlorophenols, and penta-chlorophenols. Except for 2-chlorophenol, which is a liquid at room temperature, all of the chlorophenols are solids. The chlorophenols have a strong medicinal taste and odour; small amounts in the range of ppb to mg l^{-1} can be tasted in water. Very small amounts of chlorophenols can also make fish to taste bad [30]. Chlorophenols with at least two chlorines have been either used directly as pesticides or converted into pesticides. Also, chlorophenols, especially 4-chlorophenol, have been used as antiseptics. In addition to being produced commercially, small amounts of some chlorophenols, especially the mono- and di-chlorophenols, may be produced when waste water or drinking water is disinfected with chlorine, if certain contaminants are present in the raw water. They are also produced during the bleaching of wood pulp with chlorine when paper is being produced.

Sulfolane has been traditionally used in the extraction of BTX and in the removal of acid gases from a natural gas stream. Due to its combination of physical and chemical properties, sulfolane has been used in a variety of applications including as an extraction distillation solvent, polymer solvent, polymer plasticizer, polymerisation solvent and in electronic/electrical applications [31].

Nitroaromatic hydrocarbons (e. g. nitrobenzene, nitrophenols, aniline, etc.) are anthropogenic and are released into the environment in large quantities as they are widely used for manufacturing pesticides, explosives, dyes, pharmaceuticals and plastics. Nitrobenzene is an aromatic ring compound that is the major chemical intermediate required in the production of aniline (more than 98% of U.S. nitrobenzene production is used for aniline production). Additionally, nitrobenzene is used in the production of some pesticides, rubber-related chemicals, and pharmaceuticals (including acetaminophen) [32]. The current use pattern of p-nitrophenol is as follows: production of N-acetyl-4-aminophenol, 55%; exports, 35%; miscellaneous other uses including leather tanning, insecticides (methyl and ethyl parathion), dyestuff and oxydianiline manufacture, 10%. Small amounts of p-nitrophenol are used as a laboratory reagent (e.g., phosphatase and carboxyesterase determinations) and as a fungicide in military footwear [33]. Aniline is used as solvent in manufacture resins, varnishes, perfumes, shoe blacks; as component of printing inks, cloth marking and paint removers. It is also used in the synthesis of explosives, rubber accelerators, isocyanates, herbicides, and fungicides, in the synthesis of intermediates for artificial sweeteners and in the synthesis for hydrogen peroxide as catalysts and stabilizer and in cellulose production as a precursor [34].

Lastly, the family of LAS [29, 35] is used in general as detergent, as dispersant, and as anionic surfactant. Pure LAS is used mainly in dentifrice products, in hair shampoos, and in emulsion polymerisation. The rest is either used in special cosmetic formulations, e.g. for bubble baths and hair bleaches, or as a fine chemical, e.g. denaturing agent in gel electrophoresis. Technical grade LAS is used as detergent in dish-washing products (main use), as additive for plastics and lattices, and in paints and lacquers. Due to its broad use in consumer products it is expected that most of the substance will ultimately end up in the environment. The world production of LAS is estimated [35] in 2 MM of metric tons per year and its primary use is in the cosmetics/personal care product industry.

I.5. Available Technologies to Treat the Model Compounds

Nowadays, several technologies are available and have shown to be effective in treating a variety of refractory and complex effluents. These technologies can be mapped [36] (Figure I.7) for their applicability with effluent COD concentration (measured as TOC) and effluent flow rate ($m^3 h^{-1}$). The map outlines the areas where technologies are most effective. As it can be seen from the map, biological treatment is the most versatile technique. However, for refractory compounds, biological processes do not always give satisfactory results, because those organic substances are inhibitory, toxic or simply resistant to biological treatment.

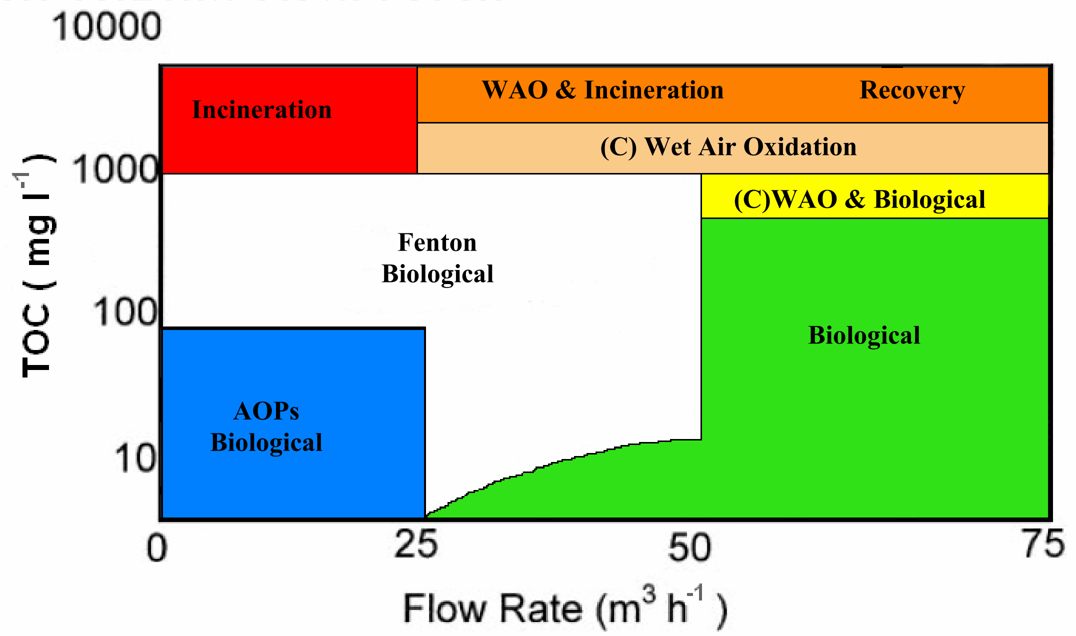


Figure I.7. Technology Map (adapted from [36])

Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO), use temperature and pressures over 120ºC and 10 bar and air or oxygen as oxidant. Fenton-like process benefits from using H_2O_2 as a liquid oxidant and a homogeneous or heterogeneous catalyst to enhance the oxidation conditions. Advanced oxidation processes (AOP) such as ozonation, photocatalysis and electrochemical oxidation (among many others), utilise electron beams, UV light or ultrasound pulses to obtain high oxidation rate through the generation of free OH radicals (mainly hydroxyl radicals). Incineration is an appropriate technology for effluents having TOC >100 g l^{-1}, but it have a extremely high energetic cost and it is not environmental friendly due to the dust dissemination to the atmosphere and to the related problems associated with dioxins production [37]. Another alternative is the recovery of organics, but it requires additional energy costs for the facilities construction and operation. Finally, there exist combined treatments, like AOPs with biological treatment, ozonation with photocatalysis or adsorption on activated carbon with CWAO, etc.

Depending on the reaction conditions two objectives can be achieved: (a) complete mineralisation of organics to CO_2 and H_2O or (b) only an increase of the effluent biodegradability by adjusting the conversion of toxic organic matter to the formation of biodegradable by-products such as carboxylic acids [38].

The first option might become extremely cost-intensive. In fact Marco et al. 1997 [39] said that investment cost for biological processes may range from 5 to 20 times less than those of chemical processes such as ozonation or hydrogen peroxide oxidation, while treatment cost may range from 3 to 10 times less. Therefore the second option seems to be the most reasonable way to solve the recalcitrant pollution problems in a cost-competitive way, if coupled before a biological treatment.

As the interest of this work is to integrate WAO/CWAO with a following biological process to deal with recalcitrant effluents, the remaining sections of this chapter will deal with a description of WAO/CWAO technologies, the state of the art in the use of these techniques as pre-treatment for biological processes, and finally the last section will show a brief description of the available techniques to measure biodegradability enhancement.

I.6 Wet Air Oxidation

Wet oxidation traces back to the 1930s, when F.J. Zimmermann, founder and namesake of Zimpro Products (now USFilter Zimpro) and its high-profile technology, Zimpro® wet oxidation, developed the process [40]. Zimmermann and his staff took spent pulping liquor from a local paper mill to produce artificial vanilla flavouring (vanillin) by partial oxidation of ligno-sulfonic acids. Zimmermann and his colleagues perfected the wet air oxidation process (or the “Zimmermann Process” as it was known), and expanded it to other applications, including wastewater treatment. Since then, applications for wet oxidation have become as varied as its history is long.

Wet air oxidation involves the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperatures (125-320 ºC) and pressures (5- 200 bar) using a gaseous source of oxygen (usually air). Enhanced solubility of oxygen in aqueous solutions at elevated temperatures and pressures provides a strong driving force for oxidation. The elevated pressures are required to keep water in the liquid state. Water also provides a medium for heat transfer and removing excess heat by evaporation. WAO has been demonstrated to oxidize organic compounds to CO_2 and other innocuous end products. The higher the temperature is the higher the extent of oxidation achieved, being the effluent mainly low molecular weight oxygenated compounds, predominantly carboxylic acids. The degree of oxidation is mainly a function of temperature, oxygen partial pressure, residence time, and the easiness of oxidation of the pollutants under consideration. The oxidation conditions depend on the treatment objective. For instance, in the case of sewage sludge, mild oxidation conditions can be used to achieve 5-15% COD reduction resulting in a sludge which is sterile, is biologically stable, and has very good settling and drainage characteristics. On the other hand, in the case of oxidation of caustic scrubbing liquors, more than 99.9% of the waste components are oxidized [37].

I.7. Catalytic Wet Air Oxidation

CWAO enhances the possibilities of WAO as it permits to work at lower temperatures and pressures. CWAO of aqueous solutions of organic compounds has demonstrated its effectiveness when the organic concentration is too low to permit an economic recovery as expressed by Mishra et al. [37] and Levec and Pintar [41]. Thus, CWAO appears as an economically and ecologically promising technique to convert refractory organic compounds into carbon dioxide or harmless intermediates at mild pressure and temperature conditions. Batch and semi-batch approaches have previously been studied by Sadana and Katzer [43], Ohta et al. [44] and Pintar and Levec [45]. Pintar and Levec [46], Fortuny et al. [48] and Levec and Pintar [41] reported that continuous process using a three-phase reactor in trickle bed regime is suitable in milder conditions for the catalytic treatment of aqueous solutions with pollutant loading because its low liquid to catalyst ratio minimises the undesired parallel reactions and polymerisation problems.

In the Catalytic Wet Air Oxidation (CWAO) both homogeneous and heterogeneous catalysts have been studied, although in practice the only highly active homogeneous catalyst is the copper ion as demonstrated by Imamura [42]. However, homogeneous catalysts suffer from the drawback that a separation step, such as precipitation, is needed to remove or recover the catalyst from the final effluent. In view of this, heterogeneous catalyst systems seem to be more promising for wastewater treatment processes. In this way, a variety of heterogeneous catalysts such as pure or mixed metal oxides [43-53] have been tested.

Non metal based materials as activated carbon (AC) [54] have demonstrated to possess catalytic activity. AC shows good properties as adsorbent for both organic compounds and oxygen. Also, it is well known that AC can perform as true catalyst for different reactions as demonstrated by Coughlin [55] or Pereira [56].

However, if only CWAO processes are considered, AC has been referenced very few times as direct catalytic matter by Fortuny et al. [50, 57], Tukac and Hanika [58], Eftaxias et al. [59, 60], Santos et al. [61] and by Suárez-Ojeda et al. [113].

In the last decade, our group investigated the performance of activated carbon catalyst for the WAO of phenol [50, 54, 57, 59, 62]. Fortuny et al. [54] compared phenol conversion, when using activated carbon and copper catalysts (Cu0803). The experimental data was obtained from a continuous trickle bed reactor using air as oxidant at different temperatures (120–160ºC) and oxygen partial pressures (6–12 bar). In ten days runs, Cu0803 was found to loose its activity due to the leaching of the copper phase. On the other hand, AC also exhibited a continuous drop in phenol conversion, finally reaching about 48% (30% with Cu0803). However, the loss of AC efficiency could be ascribed to its consumption during the experiment, thus the absolute activity of AC remained stable during the long term run. The authors have found that the oxidations of phenol and of carbon are the competitive reactions.

Also, a detailed reaction network for the catalytic wet air oxidation (CWAO) of phenol on a $CuO/\gamma\text{-}Al_2O_3$ and on a commercial activated carbon as catalyst was proposed by Eftaxias et al. [62]. The reaction network proposed accounts for all detected intermediate products of phenol oxidation overcoming the usual lumping of compounds. The model is composed by several consecutive and parallel reactions. Simple power law as well as Langmuir–Hinshelwood (L–H) expressions accounting for the adsorption effects were checked in the modelling of the reaction network. A robust non-linear multiparameter estimation approach called simulated annealing was used to simultaneously evaluate the high number of model parameters (up to 38). The simple power law model with first order dependence on both phenol and oxygen concentration predicted satisfactorily the experimental data over the entire range of operating conditions studied. Instead, when L–H expressions are incorporated for the intermediate reaction steps, the model accurately describes all the experimental concentration profiles, giving mean deviations below 8%. In addition, all estimated parameters have physical meaning. In particular, activation energies mostly agree with those reported in the literature.

I.8. Catalytic Wet Air Oxidation as precursor for biotreatment

As complete mineralisation would be excessively costly, the interest is to integrate CWAO with following biological process. In this way, a core study integrating WAO with biotreatment was done by Mantzavinos et al. [63], by Otal et al. [64] and by Patterson et al.

[26]. 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. Finally, Donlangic and Levec [65] in a recent study reported that CWAO yields products more biodegradable than WAO as a pre-treatment step. Thus, even in the case of non-toxic pollutants, the integration is advantageous.

I.9. Available methods to measure biodegradability

In the literature review, the usual performed tests to measure biodegradability are the biochemical methane potential (BMP) test, BOD_5-5 days test or a comparison based on BOD_5/COD ratio. But all these procedures are time consuming, or they cannot establish the biodegradability, toxicity or inhibitory effects immediately and accurately, so its implementation to monitor and control a Wastewater Treatment Plant (WWTP) is almost impossible. Also, the drawbacks of using BOD for assessing the aerobic biodegradability of organic compounds [41] are well known. The limitations of the BOD test mainly arise from the fact that the microorganisms may not be adapted to utilise the organic compounds tested, while the rate of biodegradability (BOD_5/COD ratio) also appears to vary with its concentration.

On the other hand, respirometry is a widely used technique to characterise wastewater, 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 [66]. Also, this technique can be applied and is used nowadays to control and monitoring WWTP [67]. To the best of my knowledge, this technique has never been used before to test the biodegradability, toxicity or inhibition effects of WAO or CWAO effluents.

Respirometry is the measure and interpretation of the biological oxygen consumption rate under certain experimental conditions, i. e. the amount of oxygen per unit volume and time that is consumed by the microorganism. The measure is often displayed by means of a respirogram, i.e. a graphical representation of the respiration rate as a function of time. The oxygen consumption or respiration rate is related directly with the biomass growth and substrate removal and can serve to model, operate and control the activated sludge process [68].

The most popular respirometric technique to determine the toxicity of a certain compound was promoted by Volskay et al. [69] and consists in comparing only the values of the slope in the dissolved oxygen (S_O) profiles obtained after adding a substrate or control pulse and after adding a pulse formed by substrate plus the possible toxic. On the other hand, Kong et al. [70] proposed another method that considers all S_O profile (not only the slope) with a commercial respirometer named RODTOX.

In this study, the technique recently developed by Guisasola et al [71] is used. In this method the difficulties due to the biodegradability of toxic compounds are avoided and give more information about toxicity, inhibition effects and biodegradability than any other techniques found in the literature. A detailed description can be found in Chapter V.

CHAPTER II. HYPOTHESIS AND OBJECTIVES

II.1. Hypothesis

CWAO could produce effluents more biodegradable than the original refractory and toxic compounds, so a subsequent conventional activated sludge treatment could be applied. Moreover, the combination of both processes can reduce the size and cost of the detoxification than either process alone. In this way the following assumptions are made:

- The use of a catalyst, especially activated carbon in CWAO process allows employing milder temperatures and pressures to oxidise refractory contaminants in water. This has been already proven for phenol [54] and its applicability to other organic compounds will now be proved.
- When both operations can be applied, chemical oxidation is more costly than biological oxidation.
- Biological oxidations are not effective for recalcitrant contaminants at high concentrations or for complex mixtures.
- Partial oxidation of recalcitrant contaminants yields increasing biodegradable reaction intermediates.

Therefore, the CWAO of recalcitrant contaminants followed by a biological completion of the contaminant oxidation will provide more effective and less expensive contaminant conversion. So, I will expect that for destruction of moderated amounts (up to 5 g l^{-1}) of substituted phenols in water, an oxidation sequence (CWAO followed by biological) can be better than any step alone. Also, I will establish the biodegradability, toxicity or inhibition rate of these compounds by respirometry before and after the CWAO treatment to find out the behaviour of the non-acclimatised and acclimatised activated sludge. Finally, I will use CWAO and an activated sludge biological oxidation, individually and in sequence, to determine the respective process efficiencies for oxidative conversions of substituted phenols contaminants.

II.2. Objectives

The main objective of my research is to develop an effective combined chemical plus biological treatment for industrial wastewater containing refractory compounds. To follow this emerging concept, I propose a technology that combines a first step of chemical oxidation (CWAO) with activated carbon as catalyst, followed by a classical biological treatment with activated sludge.

Based on this, I divide the whole doctoral research into three specific goals. The first goal was to demonstrate the feasibility of using AC as catalyst in the CWAO for other model compounds among phenol. Later, as second stage in this research, the aim was to find the optimal severity of CWAO step, in terms of substrate removal, AC catalyst preservation and biodegradability enhancement, by changing the temperature and oxygen partial pressure. The biodegradability of CWAO effluents was found by respirometry and a detailed analysis of the toxicity or inhibitory effects of each one of the main intermediates detected into the oxidation route was done. Lastly, an activated sludge plant in pilot scale was designed and an acclimatisation procedure for the inoculated microorganisms was developed by increasing the organic load of CWAO effluents in the influent to the pilot plant. The ultimate goal in the last stage of this research was to demonstrate the viability of coupling an initial CWAO step to a municipal aerobic wastewater treatment plant. Figure II.8 shows the overview of this doctoral research.

Each chapter is written in a self-contained manner. In this way, the reader will find the necessary information to evaluate the results presented in each section.

Chapter III aims to demonstrate the feasibility of conducting CWAO in a continuous fixed bed reactor operating in trickling regime, using a commercial AC as catalyst. Besides phenol, several model compounds were selected such as o-cresol, 2-chlorophenol, p-nitrophenol, aniline, sulfolane, nitrobenzene and sodium dodecylbenzene sulfonate (DBS).

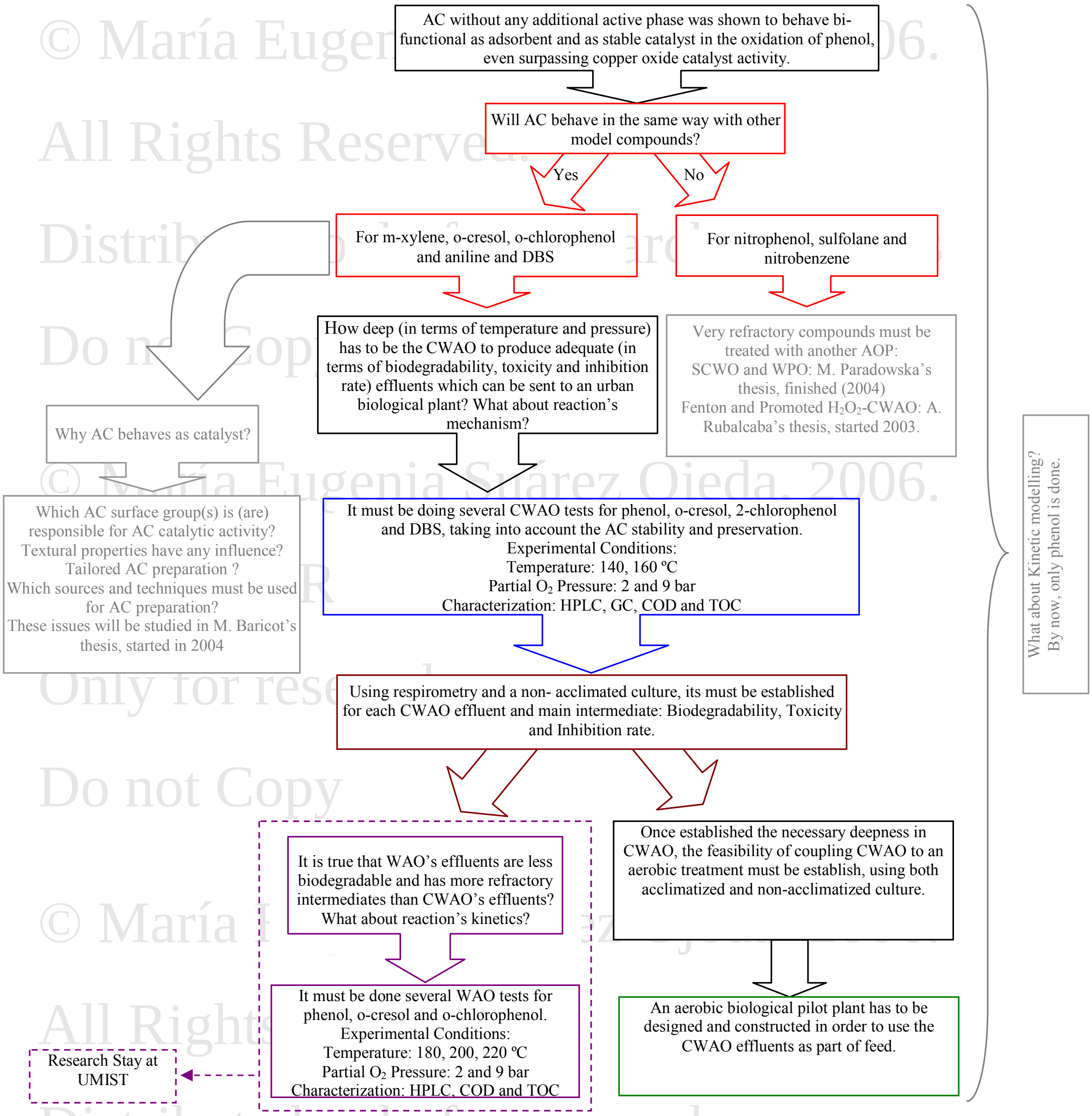
Chapter IV presents the results of the first step towards an integrated treatment of substituted phenols (phenol, o-cresol and 2-chlorophenol) based on CWAO followed by biological treatment. To design such integrated chemical-biological systems, the knowledge of physical, chemical and biological properties of the major reaction intermediates and the degradation extent of these compounds by each process are key points [72]. In this way, the adequate severity or synergy between each step can be assessed.

Later, Chapter V is devoted to find the relationship between biodegradability and toxic or inhibitory effects with the CWAO effluents composition. The objective is to ensure a viable coupling of the effluents coming from substituted phenols CWAO with a municipal biological WWTP. The biodegradation parameters of the CWAO effluents were achieved by means of respirometry and related to the intermediates compounds (carboxylic acids and quinone-like products) previously identified. Thus, a biological pilot plant has been designed and started up, in order to develop acclimatisation protocols to make possible the coupling of an initial CWAO step with an aerobic biological treatment to deal with industrial effluents.

Chapter VI shows the results obtained for WAO of phenol, o-cresol and 2-chlorophenol at several temperatures and pressures. The aim is to compare the biodegradation parameters of both WAO and CWAO effluents in order to identify the most suitable treatment for a coupling with a WWTP. This work has been done during the two research stays performed with Prof. Ian S. Metcalfe at University of Manchester, UK.

Chapter VII presents the results for DBS that showed a different behaviour in the CWAO reactor compared to the substituted phenols. Because of that, DBS results has been analysed in a different section, therefore, Chapter VII compare both WAO and CWAO as precursors for the biological treatment of industrial wastewater containing DBS.

Finally, Chapter VIII is devoted to outline the most important conclusions and future work.



Legend:

Other Related Thesis

Red Line: Chapter III Feasibility of CWAO of substituted phenols using AC as catalyst.

Blue line: Chapter IV: Temperature and Pressure influence in CWAO treatment of substituted phenols; Chapter VII: Comparison of DBS treatment by means of WAO and CWAO.

Brown line: Chapter V: Biodegradability enhancement and intermediates influence.

Green line: Chapter V: Feasibility of combined treatment.

Purple line: Chapter VI: Kinetics in WAO and comparison with CWAO test in term of biodegradability.

Figure II.8. Outlook of this thesis

CHAPTER III. FEASIBILITY OF CWAO OF SUBSTITUTED PHENOLS USING AC AS CATALYST

Some parts of the material appearing in this chapter has been used to write the article: Suárez-Ojeda, M. E.; Stüber, F.; Fortuny, A.; Fabregat, A.; Carrera, J.; Font, J. Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst. Applied Catalysis B: Environmental, 2005, 58, 105-114.

Outlook

Continuous Catalytic Wet Air Oxidation (CWAO) was investigated as a suitable precursor for the biological treatment of industrial wastewater that contained phenols (phenol, o-cresol, 2-chlorophenol, p-nitrophenol), aniline, sulfolane, nitrobenzene or sodium dodecylbenzene sulfonate (DBS). Seventy-two hour tests were carried out in a fixed bed reactor in trickle flow regime, using a commercial activated carbon (AC) as catalyst. The temperature and total pressure were 140ºC and 13.1 bar, respectively. The influence of hydroxyl-, methyl-, chloride-, nitro-, sulfo- and sulfonic- substituents on the oxidation mechanism of aromatic compounds, the occurrence of oxidative coupling reactions over the AC, and the catalytic activity (in terms of substrate elimination) was established. The results show that the AC without any supported active metal behaves bifunctionally as adsorbent and catalyst, and is active enough to oxidise phenol, o-cresol, 2-chlorophenol and DBS, giving conversions between 30 and 55 % at the conditions tested. The selectivity to the production of carbon dioxide was considerable with total organic carbon (TOC) abatement between 15% and 50%. The chemical oxygen demand (COD) reduction was between 12 and 45%. In turn, aniline, sulfolane, p-nitrophenol and nitrobenzene conversions were below 5% and there was almost no TOC abatement or COD reduction, which shows the refractory nature of these compounds.

III.1. Introduction

Fresh and unfrozen water on the Earth constitutes only 0.65% of the hydrosphere, which is mostly groundwater (0.62%). Only 0.03% is surface water in lakes, rivers, soil and the atmosphere [1]. When it is used, water becomes contaminated with a wide variety of substances. For instance chemical industries generated in the EU 5.8 million tons of hazardous wastewater composed by aromatic compounds. From this quantity, 23% are phenol–like wastewater [25]. Given these large quantities of contaminated water, effective wastewater treatment processes are becoming mandatory.

In recent years, Catalytic Wet Air Oxidation (CWAO) has been increasingly focused on the treatment of biologically refractory organic compounds because it can operate at mild temperature and pressure conditions, which has a positive effect on the economics of the treatment. Unfortunately, the lack of stable and active catalysts is a serious drawback, which prevents a wider industrial implementation [37, 73, 74].

Because of its unique properties, activated carbon (AC) has been extensively used not only as an adsorbent but also as a catalyst support or even a direct catalyst [75]. In particular, AC has often been used as a support for active metals dedicated to CWAO [76-81]. It is also well known that AC alone can perform as a true catalyst for several reactions [55, 56]. However, the potential of AC, in the absence of an active metal, as direct catalytic material for CWAO has only been recently proved for the destruction of phenol and other bioxenotic organic compounds [54, 58, 61]. It is noticeable that it performs better than other supported catalysts based on transition metals [73]. This better performance could be due to the phenol adsorption capacity of the AC that may enhance the oxidation environment conditions. Nevertheless, the performance of different ACs can be significantly different [57], which strongly suggests that not only adsorption but other specific characteristics of the ACs affect their behaviour in CWAO. In all the above studies using AC [54, 55, 58, 57, 61], the only compound tested was phenol and less attention was devoted to other reluctant organic compounds, even using metal supported catalyst [78-81].

The present chapter aims to demonstrate the feasibility of conducting CWAO in a continuous fixed bed reactor using AC as catalyst. Besides phenol, several model compounds were selected such as o-cresol, 2-chlorophenol, p-nitrophenol, aniline, sulfolane, nitrobenzene and sodium dodecylbenzene sulfonate (DBS). DBS was chosen as a representative of the linear alkylbenzene sulfonate (LAS) family. The tests were conducted at 140ºC and 13.1 bar of air, corresponding to 2 bar of oxygen partial pressure, in a fixed bed reactor operating in trickle flow regime. The performance was tested for 5 days so that the evolution of the catalytic activity could be checked. The ACs used were further characterised to highlight the role of AC into the reaction mechanism.

III.2. Experimental

III.2.1. Materials

Aldrich provided analytical grade phenol, o-cresol, 2-chlorophenol, p-nitrophenol, aniline, sulfolane, nitrobenzene and DBS. Table III.7 summarises the molecular weight, pKa, solubility and purity of the model compounds. Deionised water was used to prepare all the solutions. Feed concentrations were taken as 5 g/l for all the model compounds. For prepare high performance liquid chromatography (HPLC) mobile phases, HPLC grade methanol (Aldrich) and ultra-pure water (Millipore Direct-Q system) were used. The synthetic air used as oxidant in CWAO experiments has a purity of 99.995% (Carburos Metálicos, Spain).

The AC used as catalyst was supplied by Merck (reference #102518) in the form of 2.5 mm pellets. Table III.8 shows some of the characteristics of this AC. Prior to use, AC was crushed and sieved. Then, the particle size chosen was 25-50 mesh (0.7-0.3 mm) to optimise both pressure drop and internal mass transfer limitations, according to the work done by Stüber et al. [82]. Later, this fraction was washed to remove all the fines and finally dried overnight at 105ºC, cooled and stored under inert atmosphere until it was used.

Table III.7. Molecular weight (MW), pKa [83] and solubility [84] of the model compounds.

Compound	MW	pKa	Solubility($g\ l^{-1}$ @ 20ºC)	Purity (%)*
aniline	93.13	4.63	34	99.5
phenol	94.11	9.89	90	99.0
o-cresol	108.14	10.20	20	99.0
sulfolane	120.17	12.90	1266	99.0
nitrobenzene	123.11	3.98	1.9	99.0
2-chlorophenol	128.56	8.48	15.5	99.0
p-nitrophenol	139.11	7.15	16	98.0
DBS	348.48	7**	10	98.0

* As received from Sigma-Aldrich Corporation, Spain
** Experimental pH value of 5 $g\ l^{-1}$ DBS solution

Table III.8. Physical characteristics of the AC.

Source	Wood
Ash (%)	4.5
BET Surface area ($m^2\ g^{-1}$)	1481
micropore volume ($cm^3\ g^{-1}$)	0.3428
BJH cumulative surface area ($m^2\ g^{-1}$)*	304
pH_{PZC}	8.05

* between 17 and 3000 Å

III.2.2. Experimental set-up and procedures

CWAO experiments were carried out in a trickle bed system in down-flow co-current. The reactor containing the AC packed bed consists of a titanium tube (20 cm long and 1.1 cm i.d.), which is placed in a controlled temperature oven (±1ºC). Typically, 7.0 g of AC was loaded into the reactor. The liquid flow rate was set to give a space time of 0.12 h, i.e. a liquid weight hourly space velocity (WHLV) of 8.2 h^{-1}. Synthetic air was used as oxidant at a total pressure of 13.1 bar corresponding to an oxygen partial pressure of 2 bar. The air flow rate was kept constant at 2.4 ml s^{-1} in standard conditions, which is well beyond the stoichiometric oxygen uptake needed. The experiments were run at 140ºC for 72 h. Liquid samples were periodically withdrawn and then analysed to determine substrate conversion (X), COD reduction (X_{COD}) and TOC abatement (X_{TOC}).

Data acquisition of reactor temperature, reactor inlet and outlet pressures and liquid flow were performed with Field Point modules from National Instruments Spain®. Data handling and recording were performed with a virtual instrument programmed in Labview 7.1® also from National Instruments Spain. Figure III.9 shows a schematic draw of the CWAO system, whereas Figure III.10 shows a detailed scheme of the CWAO reactor.

The same experiment was conducted twice to check the reproducibility of results and the match (within ±5%) between successive experiments was excellent. The data reported in the paper are the arithmetic average of the results derived from repeated CWAO experiments.

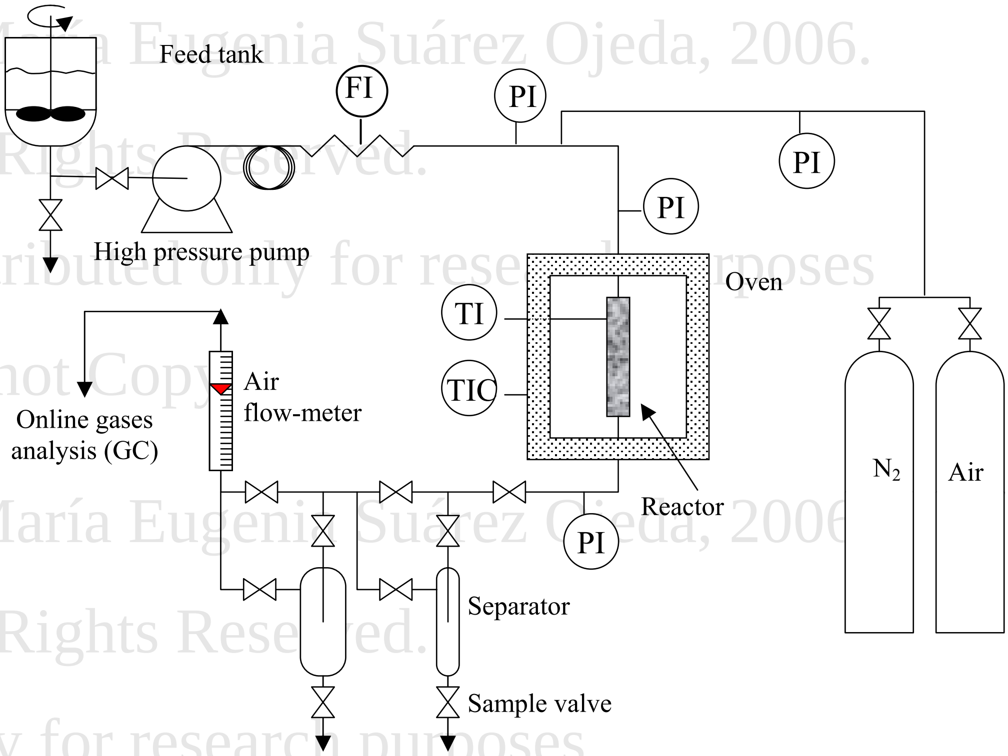


Figure III.9. CWAO Schematic diagram.

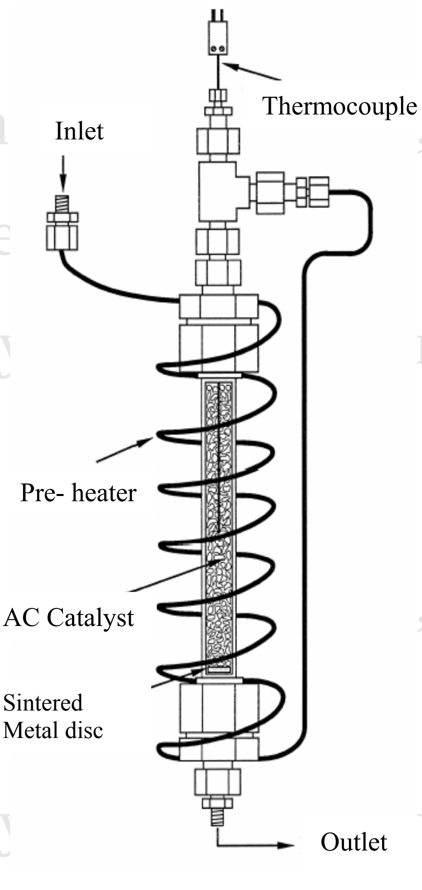


Figure III.10. Detailed schematic draw of CWAO reactor

Sample concentrations of substituted phenols and sulfolane were immediately determined by gas chromatography (GC 6890, Agilent Technologies). The chromatograph was equipped with an HP-5 capillary column (5% phenyl-methyl-siloxane, 30 m x 0.32 mm ID x 0.25 µm film thickness). The same analytical protocol served to quantify substituted phenols and sulfolane. An isothermal (40ºC) program was applied for the first 6.3 min, then the temperature was increased by 20°C/min for 3 minutes, and finally the heating rate was changed to 30ºC/min until the temperature reached 120ºC, which was maintained constant for 1 min. After that, a ramp of 30ºC/min was applied to reach 140ºC, which was kept constant for 1 min. The last sequence increased the temperature from 140ºC to 180°C at a heating rate of 10°C/min. The FID detector was maintained at 300ºC and the injector was kept at 250ºC.

Sample concentrations of p-nitrophenol, nitrobenzene, aniline and DBS were immediately determined by HPLC (model 1100 Agilent Technologies). The analysis was performed with a C18 reverse phase column (Hypersil ODS, Agilent Technologies) and a mobile phase of methanol and water consisting of 35:65 v/v for p-nitrophenol and of 50:50 v/v for nitrobenzene. The flow rate was 1 ml min^{-1}. The wavelength in the diode array detector was 254 nm. For aniline, the mobile phase used was a mixture of acetonitrile and water (60:40 v/v), with a flow rate of 1 ml min^{-1} and a wavelength of 280 nm in the detector. The mobile phase was acidified to pH equal to 2 with concentrated sulphuric acid.

Finally for DBS, a method described by Matthijs and De Henau [85] and Patterson [86] was adapted by using an acetonitrile-water-sodium perchlorate mobile phase to separate the DBS from its reaction products. Two mobile phases were used. Solution A was a mixture of acetonitrile and water with a proportion of 70:30 v/v whereas solution B was only water. Sodium perchlorate was added to both mobile phases at a concentration of 0.15 M. Again a flowrate of 1 ml/min and a wavelength of 225 nm were used.

COD was measured with the standard method 5220D [87], whereas TOC was quantified with the method 5310B [87]. The CO_2 selectivity was calculated by balance between the initial and final TOC values in the experimental samples.

The results are compared in terms of conversion, i. e. model compound destruction. The general expression used is:

$$X(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \cdot 100 \qquad \text{Equation III.1}$$

where C_0 is the inlet concentration and C_e is the concentration in the effluent. Equation III.1 can also be used to calculate both X_{COD} and X_{TOC} in a similar way.

The classical phenol oxidation scheme proposed in the literature [88] was investigated in the phenol experiments by checking the presence of the reported intermediates. Hence, samples were subjected to a deeper analysis by HPLC to determine oxidation intermediates such as quinone-like products and organic acids. The analysis was carried out using a C18 reverse phase column (Hypersil ODS, Agilent Technologies) and a mixture of water and methanol. The gradient starts from 100% of water and goes to 50:50 v/v of water:methanolB at minute 8. It remains isocratic until the end. Both mobile phases were acidified to pH equal to 1.5 with concentrated sulphuric acid.

A complete scheme of the CWAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [48, 54, 57]. However, pictures of all analytical and reaction equipment and data acquisition system could be found in Annex I.

III.2.3. Characterisation of the activated carbon

AC adsorption isotherms for the various target compounds were obtained at 20ºC (±2ºC) in oxic conditions following a standard protocol [89, 90]. The pH in the zero point of charge (pH_{ZPC}) for the AC was determined according to Nouri et al. [91].

At the end of the CWAO test, the AC used was carefully collected and dried at 105ºC overnight under an inert atmosphere to remove the excess water. Then, the AC was divided into three parts. The first one of them was dried at 400ºC under nitrogen atmosphere to remove any physisorbed compound. This temperature was selected because all the compounds seem to be completely desorbed but AC does not undergo major reactions. Subsequently, the AC was weighed to measure the weight change (W_{AC}).

The second part (approx. 25 mg) was subjected to Thermogravimetric Analysis (TGA). The analysis was carried in a Thermobalance Perkin-Elmer model TGA7, TCA7. The sample was heated from 100ºC to 900ºC under nitrogen flow at a heating rate of 10ºC/min.

Finally, the last part (between 20 and 30 mg) was used to determine textural properties by nitrogen adsorption isotherms at 77 K in a Micromeritcs instrument model ASAP 2010. For such studies, samples were outgased at 120ºC under vacuum for 24 h. The textural properties such as surface area, micropore volume and cumulative surface area were calculated by applying different model methods i. e. BET, Harkins and Jura t-plot and Barret-Joyer-Halenda (BJH) which are included with the Micromeritics software.

III.3. Results and Discussion

The results and discussion are divided into two sections. In the first, the CWAO performance is discussed by means of X, X_{COD} and X_{TOC}. Also, the reactivity order and the reaction mechanisms are examined. In the second section, the relation between AC behaviour and the reactivity order is investigated, using adsorption isotherm data, AC weight change, TGA and data from N_2 adsorption isotherms.

III.3.1. Model Compound Disappearance

Figure III.11a shows the conversion evolution for a 72-h test at 140ºC and 2 bar of oxygen partial pressure. As previously found [57], three different zones can be distinguished in all the cases. Firstly, after starting an adsorption dominating period results in an apparent total conversion. Secondly, a continuous fall in conversion is observed when the AC bed progressively undergoes both adsorption and oxidation of the model compound. Finally, once the bed is saturated, true conversion almost attains steady state.

The adsorption dominating period lasts for about 8 h in the case of phenol, 5 h for o-cresol, 7 h for 2-chlorophenol, 7 h for DBS, 4 h for aniline and 1-2 h for sulfolane. The duration of the adsorption dominating period mostly agrees with the respective adsorption capacity and bed loading. The saturation times according to the flow-rate and adsorption capacity calculated from the Freundlich equation at 20ºC (see next section) are 10 h for phenol, 11 h for o-cresol, 16 h for 2-chlorophenol, 25 h for DBS, 12 h for aniline and 5 h for sulfolane, assuming a constant concentration through the bed. The difference between the experimental and theoretical saturation times could be due to this assumption but also to the fact that the adsorption capacity decreases as the temperature increases [92, 93]. It must be noted that adsorption isotherms were obtained at 20ºC while the experiments were done at 140ºC.

Another factor that could influence the adsorption capacity is the pH. Figure III.11b shows the pH profiles throughout the test. At the start the pH is between 6.7 and 6.8, close to neutrality, which confirms the absence of the compound in the effluent. Then the pH begins to decrease during the transient state and reaches a steady state value. This decrease is caused by the formation of organic acids (or hydrochloric acid, in the case of 2-chlorophenol) as oxidation by-products. The adsorption period occurs at pHs above 5 and a decrease in adsorption capacity has been reported above this pH for several substituted phenols. These compounds can be in undissociated and ionised forms, above a pH of 5 and it is well known that ionised forms of species adsorb less effectively onto AC than their undissociated forms do [90]. However, as shown in Table III.8, the pH_{PZC} of this AC is 8.05, therefore the AC surface is positively charged during the adsorption period and during the rest of the test; therefore, the AC surface would exhibit a high affinity for anions or ionised forms of parent compounds.

Adsorption isotherms were obtained without adjusting the pH, i. e. the solution pH was provided according to the pKa values of each compound (Table III.7). In accordance with the values, the model compounds are of an acid nature, thus the solutions pH were below the pH_{PZC}, and the electrostatic forces would increase the adsorption capacity. For these reasons, the pH does not seem to be determinant in the adsorption capacity decrease observed in the CWAO test.

The transient period lasts between 10 and 20 hours depending on the compound. In this period, the conversion goes from apparently 100% to the steady state value, and the oxidation reaction continues, producing reaction intermediates that are also adsorbed onto AC. These intermediates could compete with the compound for the active sites until a balance between them is attained, which finally results in the steady state conversion.

The steady state period corresponds to the last 30 or 40 hours in every test, depending on the compound. The steady state values of X are 55% for 2-chlorophenol, 45% for phenol, 38% for DBS, 33% for o-cresol, 6% for aniline, 5% for sulfolane and practically no conversion for nitrobenzene and p-nitrophenol. The results permit to distinguish two groups. The first one with high reactivity includes phenol, 2-chlorophenol, o-cresol and DBS, while the second one with low reactivity, includes aniline, p-nitrophenol, sulfolane and nitrobenzene.

The zero activity of nitrobenzene can be attributed to the nitro group, a very strongly deactivating group. The rather mild pressure and temperature conditions prove to be insufficient to oxidize the nitrobenzene molecule. p-nitrophenol also contains a nitro group, but has a hydroxyl group strongly activating in para position, leading to some reactivity compared to nitrobenzene. Aniline conversion (6%) is similar to that of p-nitrophenol (7%) due to NH_2 group rather activating, but on the other hand, aniline does not have OH group to make it more active. We did not find literature information to explain the conversion obtained for sulfolane (5%) by the electrophilic substitution mechanism. Sulfolane has a ring containing heteroatom (sulfur) and not a benzyl ring as the other compounds studied. For this latter group, no further study was made. Thus, the following discussion will not refer to these compounds.

Figure III.12 shows the evolution of X_{COD} and X_{TOC} for phenol, 2-chlorophenol, o-cresol and DBS. The same tendencies described for Figure III.11a can be drawn in these cases. At steady state, X_{COD} is close to 48% for 2-chlorophenol, 30% for phenol, 25% for DBS and 15% for o-cresol. For X_{TOC}, the values in the steady state are 47% for 2-chlorophenol, 21% for phenol, 24% for DBS and 14% for o-cresol.

In the case of phenol, the detailed HPLC analyses showed that the main partial oxidation products were light carboxylic acids such as oxalic, acetic and formic acids. Malonic, maleic and its isomer, fumaric acid, were detected in trace amounts. Finally, measurable amounts of hydroquinone, catechol and benzoquinones were also observed. No other possible intermediates were detected. All the intermediates detected are reported in the reaction pathway described by Devlin and Harris [88] and have also been found in previous research, using the same reactor and operating conditions [59]. The presence of these intermediates, then, suggests a consecutive-parallel reaction pathway which agrees with the simplified reaction pathway proposed by Eftaxias et al. [62].

Because of the presence of partially oxidised products, X_{COD} is lower than the respective X. It should be noted that the higher the difference between X and X_{COD} is, the higher the amount of partially oxidised products in the liquid effluent. Hence, the differences in the tests are 18% for o-cresol, 15% for phenol, 13% for DBS, and 7% for 2-chlorophenol. Therefore, 2-chlorophenol seems to undergo a deeper oxidation. This can also be confirmed by the difference between X and X_{TOC}, which gives the selectivity towards carbon dioxide. This selectivity increases as X and X_{TOC} become closer. Thus, the differences are 9% for 2-chlorophenol, 24% for phenol, 14% for DBS and 17% for o-cresol. These values indicate that complete mineralisation also depends on the substituent involved.

As found, the oxidation depends on the properties of the compound. As far as X is concerned, the experimental reactivity order is 2-chlorophenol > phenol > DBS > o-cresol > aniline, sulfolane. This reactivity order can be explained by nucleophilic aromatic substitution mechanism [94]. The substituents can be classified by their capacity to stabilise the sigma complex i.e., the benzonium carbanion. The substituents are strongly deactivating if they withdraw electrons and strongly activating if they releases electrons.

Hence, the sulfonic and chloride groups ($-SO_3H$ and $–Cl$) are strongly activating and the hydroxyl, methyl, dodecyl, sulfo and amino groups ($-OH$, $-CH_3$, $CH_3(CH_2)_5CH(CH_2)_4CH_3$, -

SO_2, and $-NH_2$) are deactivating for the nucleophilic aromatic substitution. Therefore, these compounds are expected to be destroyed in the order 2-chlorophenol > phenol > DBS > o-cresol > aniline and sulfolane, which matches the experimental results. De et al. [95] also propose this mechanism for the oxidation of phenol and 2-chlorophenol with hydrogen peroxide, which shows many similarities with the present case. At the selected temperature, the unique function of AC can be the generation of anions and oxygen radicals similar to those that occur in the oxidation with hydrogen peroxide or ozone. Then, the oxidation reaction should evolve in solution. As De et al. propose [95], whatever reactive species are involved, the rate at which they are added to the aromatic ring depends on the stabilisation of the sigma complex. Therefore, the proposal that a nucleophilic aromatic substitution as the reaction mechanism seems to be a reasonable explanation of the reactivity order found.

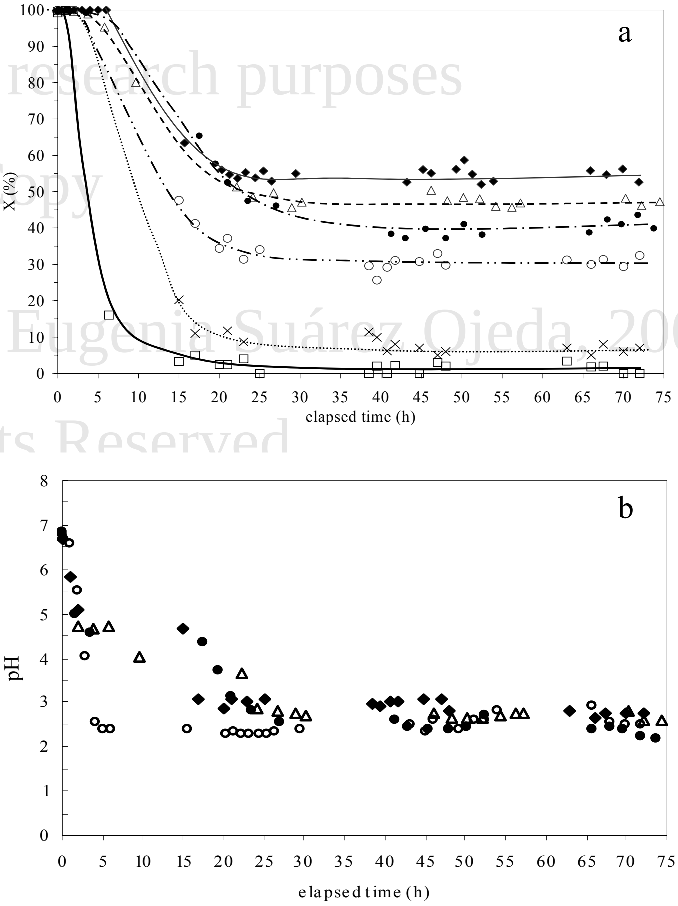


Figure III.11. X (a) and pH (b) profiles at 140ºC and 2 bar of P_{O2}. Symbols indicate experimental data {(♦) 2-chlorophenol, (Δ) phenol, (•) DBS, (○) o-cresol, (×) aniline and (□) sulfolane}. Lines show tendencies {(—) 2-chlorophenol, (--) phenol, (– –) DBS, (– ·· –) o-cresol, (····) aniline and (━) sulfolane}.

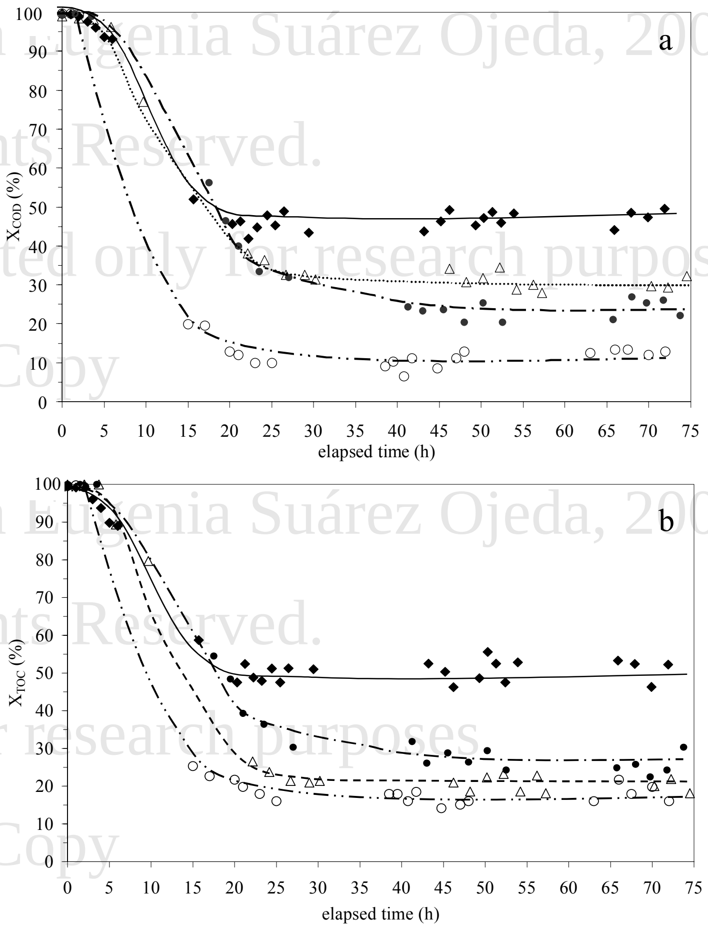


Figure III.12. X_{COD} (a) and X_{TOC} (b) profiles at 140ºC and 2 bar of P_{O2}. Symbols indicate experimental data {(♦) 2-chlorophenol, (Δ) phenol, (•) DBS, (○) o-cresol, (×) aniline and (□) sulfolane}. Lines show tendencies {(—) 2-chlorophenol, (--) phenol, (– –) DBS, (– ·· –) o-cresol, (····) aniline and (▬) sulfolane}.

However, the phenol oxidation mechanism is extremely complex and is not yet fully understood. It has been reported that the oxidation of phenol and some substituted phenols in aqueous solution by molecular oxygen is an electrophilic reaction that follows a heterogeneous-homogeneous free radical chain mechanism, where the limiting step is the reaction between the aryloxy radical and oxygen [43, 47, 96]. In this case, the easiness of oxidation to the corresponding radicals could be inferred from the half-wave potentials (HWP) of each compound [97]. The HWP refers to the relative oxidation potentials of irreversible phenol oxidations, obtained by polarographic analysis. Actually, thermodynamic redox potentials should be used for comparing oxidation rates, but these can only be measured for reversible systems and most monohydric phenol oxidations are practically irreversible because the initially formed aryloxy radicals undergo further fast reactions. Therefore, thermodynamic redox potentials for such systems cannot be determined experimentally. Nevertheless, it has been shown that polarographic HWP for irreversible systems are similar, at least in their sequence, to the actual redox potentials, so the HWP has usually been taken as a measure of oxidability of phenols [97].

The facility with which phenols can be oxidised (i.e. the formation of aryloxy radicals) increases as the steric crowding in ortho- positions and the electron-releasing properties of substituents in ortho- and para- positions increase. Table III.9 shows the HWP of the model compounds [97]. The lower the HWP is, the easier the oxidation. Therefore, for the free radical mechanism, the reactivity order should be o-cresol > 2-chlorophenol > p-nitrophenol > phenol > aniline, which does not match the reactivity order found in this study. This suggests that the presence of AC as catalyst probably modifies the classical reaction mechanism.

Table III.9. Half-wave oxidation potentials [97].

Compound	$E_{1/2}$ (mv)
o-cresol	556
2-chlorophenol	625
p-nitrophenol	924
phenol	1004
aniline	1135

III.3.2. Activated Carbon Performance

Figure III.13 shows the adsorption isotherms at 20ºC. These isotherms come from equilibration for 4 hours and were obtained in oxic conditions, i.e. the solution was always in contact with air. Thus, some degree of oxidative coupling could take place during the process as a result of the presence of dissolved oxygen [98]. Anyway, according to the literature [99], this effect should only be relevant for long exposures (over 12 hours) between the phenols and the AC, which is not the case.

These adsorption isotherms were later fitted to the Freundlich equation:

$$q = kc^{1/n} \qquad \text{Equation III.2}$$

where c is the compound concentration in bulk solution (mg l^{-1}) and q is the amount of substrate adsorbed in mg per g of AC. This empirical equation assumes that the adsorbent has a heterogeneous surface composed by different classes of adsorption sites, so as 1/n values are closer to 0 indicates heterogeneous adsorption and a 1/n values close to 1 indicates homogeneous adsorption. Table III.10 lists the parameters obtained by fitting and the adsorption capacity calculated at 5000 ppm for each compound. In Table III.4, the 1/n values are below 1, indicating a favourable adsorption onto the surface [100]. Also, it must be noted that the larger molecule (DBS, Table III.7) has a 1/n value of 0.7 being close to a homogeneous adsorption. On contrary, aniline and phenol has more or less the same molecular weight but aniline has 2 unpaired electrons which could increase the possibility for heterogeneous adsorption and therefore decreases it adsorption capacity onto the AC.

The adsorption capacity follows the order nitrobenzene > DBS > 2-chlorophenol > p-nitrophenol > aniline > o-cresol > phenol > sulfolane. It is evident that the higher the solubility in water (Table III.7) the lower the adsorption capacity is. Also, the bigger the molecule is, the higher the adsorption capacity, which agrees with the results of Daifullah and Girgis [101]. In their study, the adsorption capacity of substituted phenols is a direct function of the molecular dimension of the sorbate and an inverse function of its solubility. The same direct correlation between solubility and adsorption capacity was found by García-Araya et al. [102] for phenolic acids. Comparing the reactivity order obtained with the adsorption capacity, it can be concluded that the adsorption phenomena do not explain the CWAO performance for the different compounds tested.

Table III.10. Freundlich equation* parameters and adsorption capacity at 5000 mg l^{-1}.

Compound	q (mg g AC^{-1})	k (mg gAC^{-1})(l mg^{-1})$^{1/n}$	1/n
sulfolane	188±11	25±1	0.24±0.01
phenol	395±20	34±1	0.29±0.02
o-cresol	451±16	37±1	0.29±0.02
aniline	496±32	19±1	0.38±0.01
p-nitrophenol	612±20	99±1	0.21±0.02
2-chlorophenol	674±35	44±1	0.32±0.01
DBS	1028±44	3±1	0.70±0.01
nitrobenzene	1243±27**	37±1	0.46±0.02

* Correlation factors (R^2) are over 0.95

** At 2000 mg l^{-1} in the bulk solution

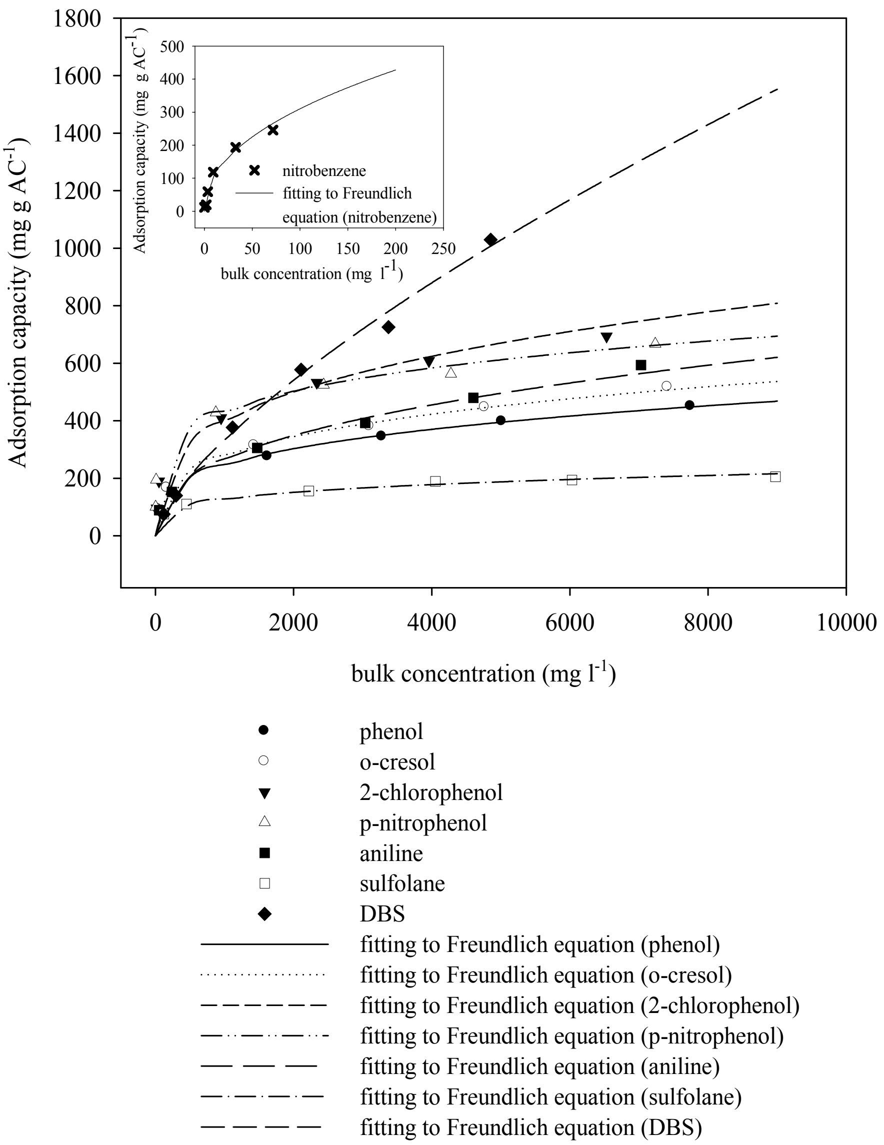


Figure III.13. Adsorption isotherms of selected model compounds. Symbols indicate experimental data, whereas lines correspond to the Freundlich model.

Because it is well known that phenolic compounds can undergo coupling reactions, the changes in the AC weight and AC surface area during oxidation should shed some light on the loss of AC catalytic activity and the influence of oxidative coupling on CWAO. Table III.11 shows the W_{AC} and textural properties for the used AC from each experiment.

Table III.11. Original bed loading, W_{AC} and textural characterization at the end of the CWAO test.

Compound	phenol	o-cresol	2-chlorophenol	DBS
Loaded AC (g)	7.60	7.30	6.90	7.01
W_{AC} (%)	3.61	6.09	7.84	6.16
BET Surface Area($m^2\ g^{-1}$)	122	24	169	285
Micropore Volume ($cm^3\ g^{-1}$)	0.003	0.001	0.004	0.006
BJH cumulative area surface($cm^2\ g^{-1}$)*	96	2	120	148

* between 17 and 3000 Å

As Table III.11 shows, W_{AC} was positive (i. e. the AC weight increased) for all model compounds by the end of the test, which is in reasonable agreement with the observations of Fortuny et al. [57] for phenol CWAO. These observations can be extended for the rest of compounds tested in this study. W_{AC} has previously been studied [54, 57] for phenol CWAO, with the same reactor and a range of conditions (temperature, pressure and space time) that includes those used here. WAC turned out to be positive or negative depending on the elapsed time and the operating conditions [54, 57]. At 140ºC and 9 bar of oxygen partial pressure, it was observed that AC weight increases in the first 24 hours, then reaches a maximum and finally decreases to values below the original one. Furthermore, after 10 days of experiment and at lower oxygen partial pressures, the AC weight increases [54].

Many studies have shown that this positive W_{AC} can be attributed to the deposition of polymeric compounds produced by oxidative coupling reactions over the AC [89, 103-105]. Cooney and Xi [90] demonstrated that, at low pHs, oxidative coupling reactions can be accelerated by the presence of a substituent on the phenol molecule. They postulated that oxidative coupling reactions occur simultaneously with the oxidation reaction and these coupling reactions probably block the active sites in AC, and decrease its catalytic activity. According to Cooney and Xi [90], oxidative coupling reactions follow the order o-cresol > 2-chlorophenol > phenol, which except for 2-chlorophenol is similar to the W_{AC} presented in Table III.11.

A minimum AC weight gain, i. e. a minimum of oxidative coupling reactions, must correspond to a maximum of X, since oxidative coupling is expected to block the active sites and diminishes the superficial area (as Table III.5 shows) and, therefore, the catalytic activity. However, as can be see it in Table III.11, the BET surface area decrease following the order DBS > 2-chlorophenol > phenol> o-cresol, which is in fact the reactivity order obtained in the experiments with the exception of DBS. Thus, according to the present results, the oxidative coupling cannot explain by itself the reactivity order found.

In order to relate W_{AC} with X, the experimental results were fitted to a first-order kinetic model for substrate concentration assuming a plug-flow model for the trickle bed reactor [54]. Hence, the apparent kinetic constant, k_{ap}, for the compound disappearance can be estimated from:

$$k_{ap} = -\frac{Q_L}{W_{cat}} \ln\left(1 - \frac{X}{100}\right) \qquad \text{Equation III.3}$$

where Q_L is the volumetric flow rate (ml h^{-1}) and W_{cat} is the AC weight (g) in the packed bed at the start of the test.

The calculated kinetic constants are 3.32±0.04 ml h^{-1} g^{-1} for o-cresol, 3.92±0.04 ml h^{-1} g^{-1} for DBS, 4.52±0.05 ml h^{-1} g^{-1} for phenol and 7.31±0.06 ml h^{-1} g^{-1} for 2-chlorophenol. The apparent kinetic constants suggest that the higher W_{AC} (i. e. the higher loss in surface area), the lower the conversion. Again, this is valid for phenol, o-cresol and DBS, but not for 2-chlorophenol, which simultaneously shows the highest conversion, the highest W_{AC} and the highest BET surface area.

TGA were performed to find out which kind of compounds could be responsible for the weight change and to evaluate the quantity of adsorbed products. Figure III.14a and Figure III.14b show the thermograms and their first derivatives (dw/dT) of the model compounds for virgin and used AC during the TGA performed between 100 and 900ºC under nitrogen flow. The virgin AC thermogram is a typical one showing an appreciable peak around 715ºC. This peak can be related to desorption of CO and CO_2 species coming from surface oxygen groups attached to AC. According to Figueiredo [106], the surface species attached to the AC are desorbed at different temperatures. Thus, from 100ºC to 300ºC, the slow release of species is due to the decomposition of such carboxylic groups as CO_2, whereas the zone between 300ºC and 900ºC can be assigned to the release of CO_2 due to the decomposition of lactones and CO from oxygen surface groups such as carboxyl, phenyl and ethyl groups.

Generally speaking, the thermograms have two zones. In the first one, between 200-300ºC, the species are slowly released; in the second one, between 300-800ºC, in which they are released continuously and rapidly. This second zone shows a marked peak, which depends on the compound used in the CWAO. The peak occurs at 577ºC for phenol, at 442ºC for o-cresol, at 542ºC for 2-chlorophenol and at 462ºC for DBS.

It is believed that the weight loss in the first zone coincides with the release of physisorbed model compounds and reaction intermediates, whereas the weight loss in the second zone corresponds to the decomposition of chemisorbed species, including the cracking of polymers from oxidative coupling reactions [107, 108].

The total weight loss (TWL) of each sample is summarised in Table III.12 for all the CWAO tests and the virgin AC. It should be noted that the highest TWL is 29.8% for 2-chlorophenol CWAO, about three and a half times greater than that of the original AC, which was only 8%. The TWL in the AC used follows the order 2-chlorophenol > o-cresol > DBS > phenol. As expected, the same inverse relation exists between X and TWL and between X and surface area, but again the AC used in the 2-chlorophenol test is an exception.

Table III.12. Total weight loss during the TGA of the virgin and used AC [1]

Virgin AC	phenol	o-cresol	2-chlorophenol	DBS
8.0	12.2	24.2	29.8	24.1

[1] In % w/w

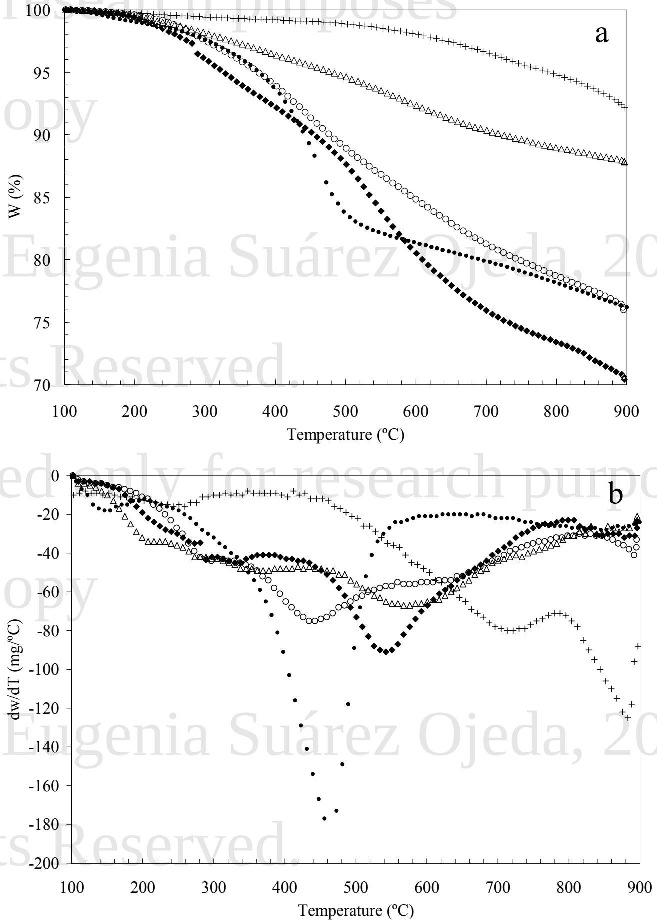


Figure III.14. TGA data (a) and first derivative of TGA data (b) of original and used AC after being tested in 72 h CWAO experiments. {(+) Virgin AC, (♦) 2-chlorophenol, (Δ) phenol, (•) DBS, and (○) o-cresol}

The W_{AC} and the TWL for each compound follow a trend that does not match the one predicted from oxidative coupling [90], so again the oxidative coupling reaction does not explain the reactivity order obtained.

A satisfactory explanation for the reactivity order in this study is still lacking, as no definitive conclusions come out from the AC characterisation done. However, the results suggest that the reaction occurs in solution instead of over the AC surface; therefore the role of AC could only be the generation of oxygen radicals and/or anions.

III.4. Conclusions

Several CWAO were performed with 2-chlorophenol, phenol, DBS, o-cresol, aniline, sulfolane, p-nitrophenol and nitrobenzene. The oxidation was conducted in mild conditions of air pressure (13.1 bar) and temperature (140ºC) in a fixed bed reactor operating in trickle flow regime. Conversions were between 30 and 55% for phenol, 2-chlorophenol, DBS and o-cresol. On the other hand, conversions were below 6% for aniline, p-nitrophenol, sulfolane and nitrobenzene. The activated carbon without any active metal was shown to have a catalytic effect on the wet oxidation of phenol, o-cresol, 2-chlorophenol and DBS. In all cases, the oxidation was highly selective to CO_2.

The reactivity order 2-chlorophenol > phenol > DBS > o-cresol > aniline, sulfolane seems to correspond to a nucleophilic aromatic substitution mechanism. Other possible factors influencing the CWAO performance such as adsorption, oxidative coupling reactions, pore blockage, etc. have been studied without obtaining a satisfactory explanation for the reactivity order obtained in this study. In the case of phenol, a detailed HPLC analysis shows intermediates that have been reported previously, which suggests a consecutive-parallel reaction pathway.

The apparent kinetic constants suggest that the higher W_{AC} is the lower the conversion is. This is true for phenol, o-cresol and DBS but not for 2-chlorophenol, which has the highest conversion and highest W_{AC} simultaneously. The positive W_{AC} can be explained by the presence of adsorbed phenolic-based polymers on the AC carbon produced by oxidative coupling reactions, as demonstrated by TGA results and nitrogen adsorption isotherms.

III.5. Acknowledgements

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CHAPTER IV. TEMPERATURE AND PRESSURE INFLUENCE IN CWAO TREATMENT OF SUBSTITUTED PHENOLS

Some parts of the material appearing in this chapter has been used to write the article: Suárez-Ojeda, M. E.; Fabregat, A.; Stüber, F.; Fortuny, A.; Carrera, J. and Font, J. Catalytic Wet Air Oxidation of Substituted phenols: Temperature and Pressure effect on the Substrate Removal, the Catalyst Preservation and the Biodegradability Enhancement. Submitted to Environmental Science and Technology, November 2005.

Outlook

The influence of oxygen partial pressure (2 and 9 bar) and temperature (140ºC and 160ºC) on continuous Catalytic Wet Air Oxidation (CWAO) of several biorefractory compounds has been investigated. The model compounds were phenol, *o*-cresol and 2-chlorophenol. Seventy-two hour tests were carried out in a fixed bed reactor in trickle flow regime, using a commercial activated carbon (AC) as catalyst. The major reaction products identified were low-molecular carboxylic acids and quinone-like products. In the case of 2-chlorophenol, chlorinated aromatics and hydrochloric acid were also found. The substrate elimination effectiveness and the occurrence of oxidative coupling reactions over the AC were studied for each compound. The results show that model compound disappearance, chemical oxygen demand (COD) removal and total organic carbon (TOC) abatement were very sensitive to temperature but almost independent of changes in oxygen partial pressure (P_{O2}). As an example, in the case of *o*-cresol CWAO at 2 bar of P_{O2}, as temperature increased from 140 to 160ºC, *o*-cresol conversion increased from 30% to 85%, COD removal from 15 to 50% and TOC abatement from 18% and 47%. Similar behaviour was found for the other model compounds tested. On the basis of these results, a possible reaction pathway and its mechanism was proposed for each model compound.

IV.1. Introduction

Industrial wastewater has a very complex composition depending on their origin, which frequently requires severe remediation treatments because of its refractory and toxic nature. Typical toxic, therefore non biodegradable, organic pollutants are phenols, surfactants, chlorinated compounds, pesticides, aryl and chlorinated alkysulfonates, polyethylene and aromatic hydrocarbons, among many others [23].

The importance of phenolic effluents, besides from their potential toxicity, is outlined by the high quantities that are eventually disposed in the environment. For instance, phenol, *o*-cresol and 2-chlorophenol are recognised toxic substances listed in the 2000 OECD List of High Production Volume Chemicals [109].

Due to the broad use of these compounds in consumer products, it is expected that high amounts of them will eventually end up in the environment. In addition, phenol is considered to be an intermediate product in the oxidation pathway of high-molecular-weight aromatic hydrocarbons.

Biological treatment of these compounds usually has low removal efficiency and a low concentration limit. As instance, microbial toxicity studies with Daphnia Magna showed that these compounds were toxics [110, 111]. Catalytic Wet Air Oxidation (CWAO) is a method for treating this kind of hazardous wastewater that is not amenable to biological treatment. CWAO is able to generate an effluent suitable to be discharged into a urban wastewater treatment plant (WWTP). Moreover, CWAO can operate at mild temperature and pressure conditions, which has a positive effect on the economics of the treatment. Unfortunately, the lack of stable and active catalysts is a serious drawback, which prevents a wider industrial implementation [37, 74].

Because of its unique properties, activated carbon (AC) has been extensively used not only as an adsorbent but also as a catalyst support or even a direct catalyst [75]. Several studies have demonstrated that AC alone can perform as a true catalyst for several reactions [55, 112], including CWAO of phenol, *o*-cresol, 2-chlorophenol, sodium dodecylbenzene sulfonate (DBS) and other bioxenotic organic compounds [54, 58, 113]. It is noticeable that AC performs better than catalysts based on supported transition metals [73]. Nevertheless, the performance of different ACs can significantly differ [57], which strongly suggests that different specific characteristics of the ACs affect their behaviour in CWAO.

Suarez-Ojeda et al. [113] demonstrated that CWAO of phenol, *o*-cresol, 2-chlorophenol, and DBS is feasible in a continuous fixed bed reactor using AC as catalyst. However, additional work is still required to determine the effect of the operating conditions on the reaction pathway and/or to elucidate other limiting factors.

This chapter presents the results of the first step towards an integrated treatment of substituted phenols based on CWAO followed by biological treatment. To design such integrated chemical-biological systems, the knowledge of physical, chemical and biological properties of the major reaction intermediates and the extent of degradation of these compounds by each process are key points [72]. In this way, the adequate severity or synergy between each step can be assessed. Therefore, several CWAO tests were done using phenol, *o*-cresol and 2-clorophenol as model compounds, at temperatures between 140ºC-160ºC and total pressure between 13.1- 49.5 bar, corresponding to 2 and 9 bar of oxygen partial pressure (P_{O2}). The aims are to determine the effect of these operating conditions on the CWAO, to give some light into the previously proposed reaction mechanism [113] and to determine the limiting factors. The following chapter will investigate the effect exerted by these operating conditions in the biodegradability and the toxicity of CWAO effluents by means of respirometric techniques.

IV.2. Experimental

IV.2.1. Materials

Aldrich provided analytical grade phenol, *o*-cresol and 2-chlorophenol. Table III.7 in Chapter 3 summarises the molecular weight, pKa, solubility and purity of the model compounds selected for this study. Deionised water was used to prepare all the solutions. Feed concentration was 5 g/l for all the model compounds. Aldrich also provided 99% pure commercial intermediates such as catechol, resorcinol, hydroquinone and *p*-benzoquinone; *o*-benzoquinone was commercially unavailable due to its instability. Acidic intermediates such as glyoxilic, oxalic, formic, malonic, acetic, maleic (and its isomer fumaric acid), succinic, acrylic, propionic and muconic (both isomers) were always between 97 and 99.5% pure commercial compounds from Aldrich. Finally, condensation products like 4-hydroxybenzoic acid, its isomer salicylic acid, salicyladehide, 1-indanone, 1,3 benzodioxole, 2,2'-biphenol and 2,4 dichlorophenol were between 98 and 99% pure commercial compounds from Aldrich. Mobile phases for high performance liquid chromatography (HPLC) were HPLC grade methanol (Aldrich) and ultra-pure water (Millipore Direct-Q system). The synthetic air had a purity of 99.995% (Carburos Metálicos, Spain).

The AC used as catalyst was supplied by Merck (reference #102518) in the form of 2.5 mm pellets. The characteristics of this AC can be found elsewhere [113]. Prior to use, AC was crushed and sieved. Then, the particle size chosen was 25-50 mesh (0.7-0.3 mm) to optimise both pressure drop and internal mass transfer limitations [82]. Later, this fraction was washed to remove all the fines and finally dried overnight at 105ºC, cooled and stored under inert atmosphere until use.

Chemical oxygen demand (COD) and total organic carbon (TOC) analysis were measured following the standard methods 5220D and 5310B [87].

IV.2.2. Experimental set-up and procedures

A complete scheme of the CWAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [Chapter 3, annex I or references 48, 54, 57, 113].

Air was used at a total pressure between 13.1 and 49.5 bar corresponding to a P_{O2} of 2 and 9 bar at each temperature. The experiments were run at 140ºC and 160ºC for 72 h. Liquid samples were periodically withdrawn and analysed to determine model compound disappearance (X), COD reduction (X_{COD}), TOC abatement (X_{TOC}) and reaction intermediates.

As in the previous chapter, the results were compared in terms of conversion, either X, X_{COD} and X_{TOC}. The general expression used is:

$$X(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \cdot 100 \qquad \text{Equation IV.4}$$

where C_0 is the inlet concentration and C_e is the outlet concentration.

The same experiment was repeated at least twice to check the reproducibility. The matching between successive experiments was excellent (within 5%). Data reported are the average from repeated CWAO experiments.

According to the oxidation pathways proposed in the literature for each model compound [88, 95, 96, 114-118], a set of known intermediates were checked in order to elucidate the reaction pathway. Quinone-like compounds, condensation products and organic acids were separated by HPLC. The analysis was carried out using a C18 reverse phase column (Hypersil ODS, Agilent Technologies) and a mixture of ultra-pure water (phase A) and methanol (phase B). The gradient started from 100 % of A and progressively changes to 50:50 v/v of A:B in 25 minutes, then it remained isocratic until minute 37. Both mobile phases were acidified to pH equal to 1.5 with concentrated sulphuric acid. A HPLC chromatogram from a standard calibration mixture is shown in Figure IV.15 whereas the retention times are in Table IV.13.

For phenol samples, the intermediates considered were in part reported in the reaction pathway described by Devlin and Harris [88]: glyoxilic acid, oxalic acid, formic acid, malonic acid, acetic acid, maleic acid (and its isomer fumaric acid), succinic acid, acrylic acid, propionic acid and muconic acid (both stereoisomers), hydroquinone, catechol and *p*-benzoquinone. In addition, 4-hydroxybenzoic acid (4-HB), its isomer salicylic acid (2-HB) and resorcinol were also calibrated.

For *o*-cresol samples, new partial oxidation products were added such as salicylaldehide, 1-indanone, 1,3-benzodioxole and 2,2'-biphenol which were reported by Martino et al. [118] as the most frequently found compounds in the catalytic super-critical oxidation of *o*-cresol.

Finally, for 2-chlorophenol samples, 2,4 dichlorophenol reported as intermediate in the CWAO of 4-chlorophenol over supported noble metal catalyst by Qin et al. [116] was taken into account.

Other intermediates such as methyl- and chlorinated- quinones were checked, however these intermediates were not detected in the CWAO samples, therefore, it were not included in the sample chromatogram (Figure IV.15) nor in the results section.

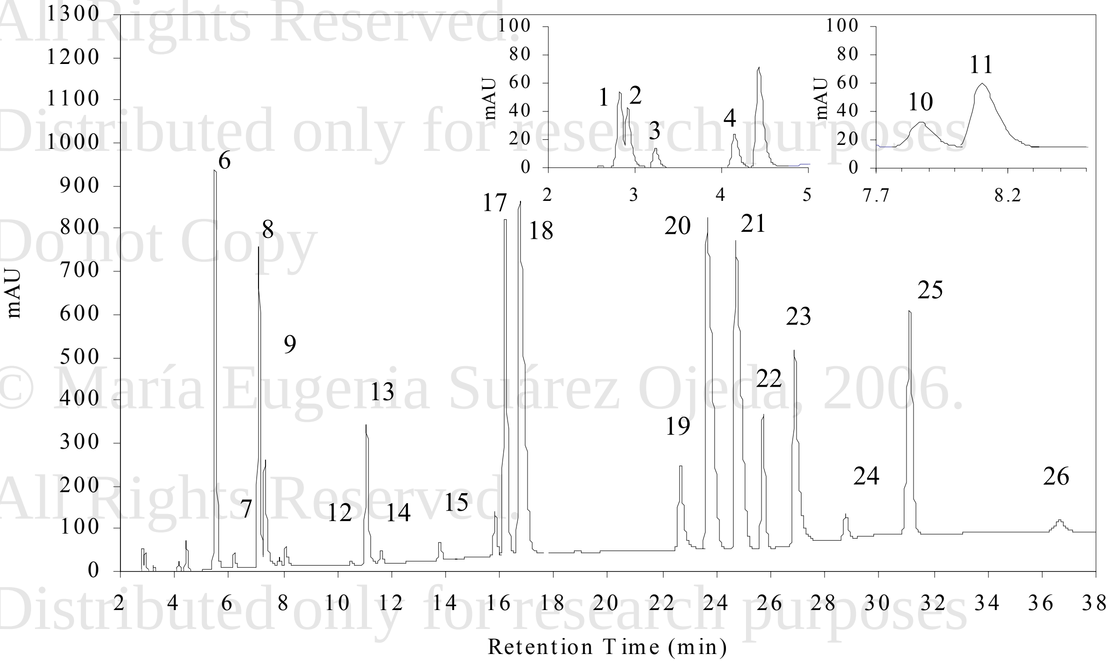

Figure IV.15. HPLC chromatogram from a standard calibration mixture.

Table IV.13. Retention times in a chromatogram from a standard calibration mixture.

Peak Number	Compound	Retention Time (min)	Wavelength (ηm)
1	Glyoxylic acid	2.826	210
2	Oxalic acid	2.923	210
3	Formic acid	3.245	210
4	Malonic acid	4.157	210
5	Acetic acid	4.433	210
6	Maleic acid	5.499	210
7	Succinic acid	6.204	210
8	Fumaric acid	7.111	210
9	Acrylic acid	7.342	210
10	Hydroquinone	7.884	254
11	Propionic acid	8.110	210
12	Resorcinol	10.547	254
13	*p*-Benzoquinone	11.091	254
14	Catechol	11.640	254
15	trans,trans-Muconic acid	13.809	210
16	cis,cis-Muconic acid	15.856	210
17	4-Hydroxybenzoic acid	16.202	210
18	Phenol	16.566	254
19	Salicylaldehide	22.688	254
20	*o*-Cresol	23.661	254
21	2-Chlorophenol	24.734	254
22	1-Indanone	25.727	254
23	Salicylic acid	26.894	210
24	1,3-Benzodioxole	28.813	210
25	2,2'-Biphenol	31.154	210
26	2,4-Dichlorophenol	36.800	210

IV.2.3. Activated carbon characterisation

The AC used in each CWAO test was carefully collected and dried at 105ºC overnight under an inert atmosphere to remove the excess water. Then, the used AC was subjected to several characterisations. A thermogravimetric analysis (TGA) was done in a thermobalance Perkin-Elmer model TGA7, TCA7. The 20 mg sample was heated from 100ºC to 900ºC under nitrogen flow at a heating rate of 10ºC/min.

The nitrogen adsorption isotherms at 77 K were obtained to determine textural properties with a Micromeritics instrument model ASAP 2010. For such studies, 20 mg samples were outgased for 24 h at 120ºC under vacuum. The textural properties such as surface area, micropore volume and cumulative surface area were calculated by applying different model i. e. BET, Harkins and Jura t-plot and Barret-Joyer-Halenda (BJH) which are included with the Micromeritics software.

Finally the used AC was dried at 400ºC under nitrogen atmosphere to remove any physisorbed compound. Subsequently, the AC was weighed to measure the mass change (M_{AC}) as following:

$$M_{AC}(\%) = \frac{\left(M_{AC}^{f} - M_{AC}^{0}\right)}{M_{AC}^{0}} \cdot 100 \qquad \text{Equation IV.5}$$

where M_{AC}^{0} is the initial AC weight and M_{AC}^{f} is the weight of used AC after drying at 400ºC.

IV.3. Results and Discussion

This section is divided into two parts. In the first one, CWAO performance is discussed by means of X, X_{COD} and X_{TOC}. Also, the reactivity order and the reaction mechanisms are examined for each compound. In the second part, the relation between the AC behaviour and the reactivity order is investigated, using AC weight change, TGA and data from N_2 adsorption isotherms.

Several simultaneous reactions occur when using AC as catalyst in CWAO. There is not only the expected oxidation of the model compound and its intermediates, but also AC oxidation/burning and oxidative coupling reactions (or irreversible adsorption) of the compounds over the AC are occurring. Besides, physical adsorption of the substrate and of the partial oxidation products is also happening at the same time. Therefore, the use of AC as catalyst in CWAO increases even more the already intrinsic complexity of wet oxidation. These parallel reactions and adsorption processes cannot be uncoupled and studied separately. Therefore, only global information can be taken from the effluent (section IV.3.1) and used AC characterization (section IV.3.2) attempting to establish the contribution of each one in the biodegrability enhancement (chapter V).

During the discussion, the CWAO conditions will use the following nomenclature: 140-2 will refer to 140ºC and 2 bar of P_{O2}, 160-9 equals to 160ºC and 9 bar of P_{O2} and so on.

IV.3.1. Model Compound Disappearance and Reaction Intermediates

Figure IV.16 shows the conversion evolution, for a 72-h test at 140-2 and 160-2, whereas Figure IV.17 shows the conversion evolution for 140-9 and 160-9. As previously found [113], three different zones could be distinguished in all the cases. Firstly, an adsorption-dominating period resulted in an apparent total conversion. Secondly, once the breakthrough front is reaching the bottom of the reactor, a sudden fall of conversion is detected. Finally, conversion almost attained steady state.

Since the amount adsorbed over an adsorbant decreased as temperature increased [92], the adsorption period for 160ºC tests is expected to be longer than for 140ºC tests, as found. As example, the increase in the adsorption period in the 160ºC tests compared to the 140ºC test was up to 4 h for phenol and up to 10 h for both *o*-cresol and 2-chlorophenol. However, this is just a rough estimation as the actual time is greatly affected by the simultaneous oxidation of the compound, oxidative coupling phenomena and even adsorption competition with the partially oxidised products formed in the course of the test.

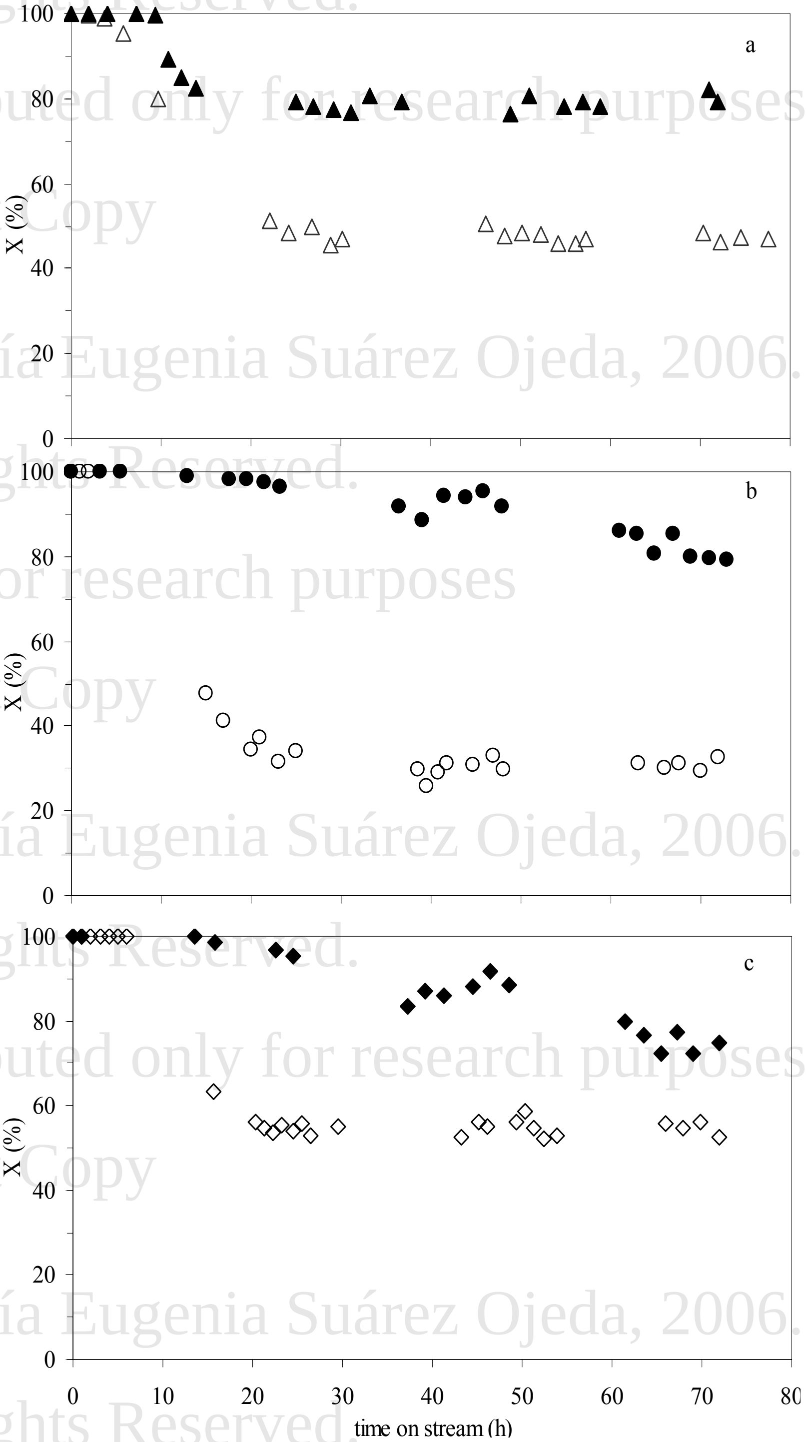

Figure IV.16. Conversion evolution in 72 hours tests at 2 bar of partial O_2 pressure and 140ºC (open symbols) and 160ºC (full symbols). Symbols indicate experimental data {a) phenol, b) *o*-cresol, c) 2-chlorophenol}.

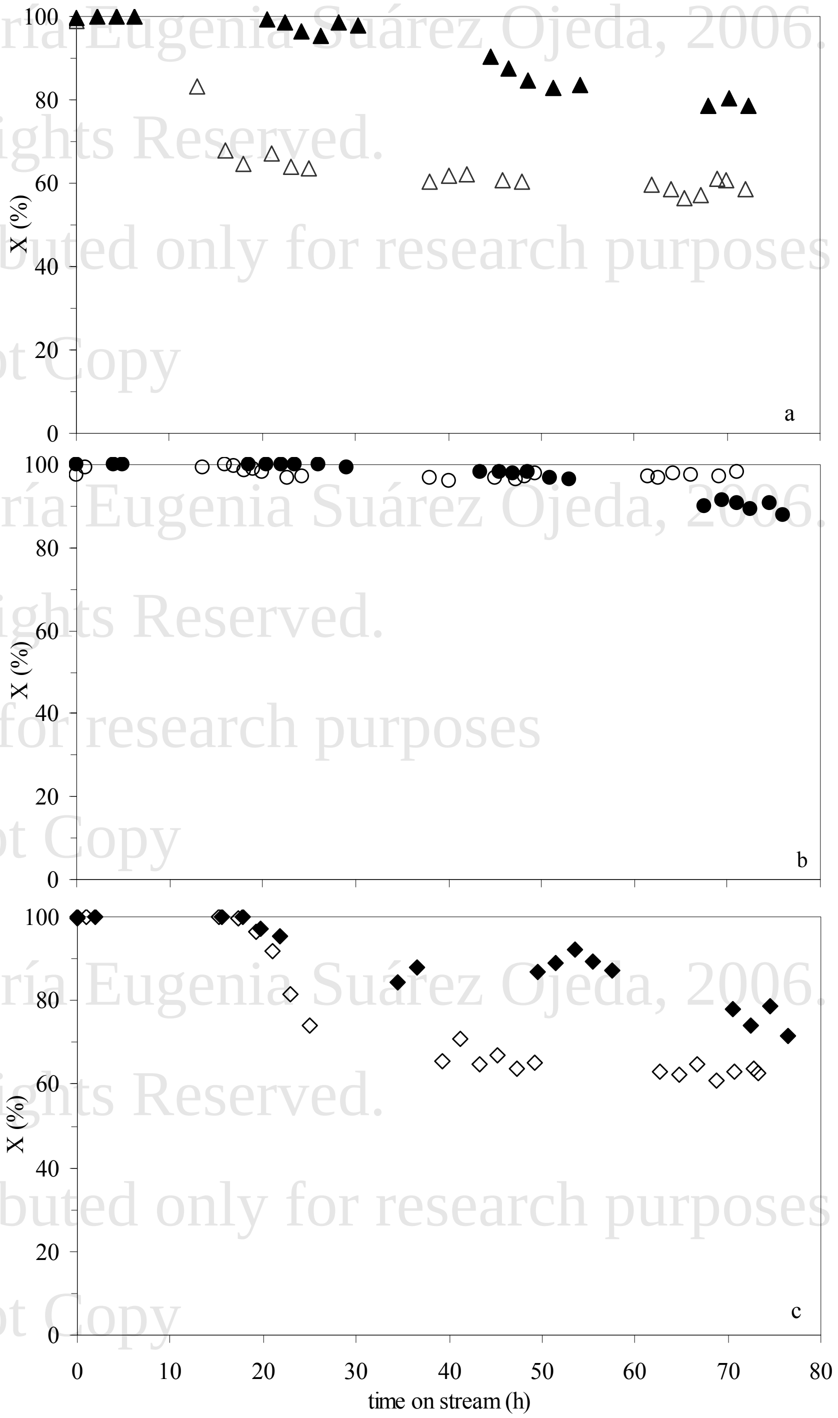

Figure IV.17. Conversion evolution in 72 hours tests at 9 bar of partial O_2 pressure and 140ºC (open symbols) and 160ºC (full symbols) bar. Symbols indicate experimental data {a) phenol, b) *o*-cresol, c) 2-chlorophenol}.

The pH profiles for CWAO tests are shown in Figure IV.20. At the beginning, the pH was between 7.0 and 6.5 which confirm the absence of the compound in the effluent; because all model compounds have an acidic nature as indicated by the pKa values presented in Table III.7 in Chapter 3. Later, the pH began to decrease during as the breakthrough front approaches the end of the reactor bed and finally reached a steady state value. This decrease is caused by the formation of partial oxidation products which are mainly carboxylic acids. In the case of 2-chlorophenol, the also formed hydrochloric acid contributes to lower the pH. The occurrence of organic acids as oxidation by-products was proved by HPLC (section IV.2.2) whereas hydrochloric acid was detected by GC as explained in chapter III.

The evolution of X_{COD} and X_{TOC} for phenol, 2-chlorophenol and *o*-cresol follows the same tendencies described for X as can be seen in, respectively.

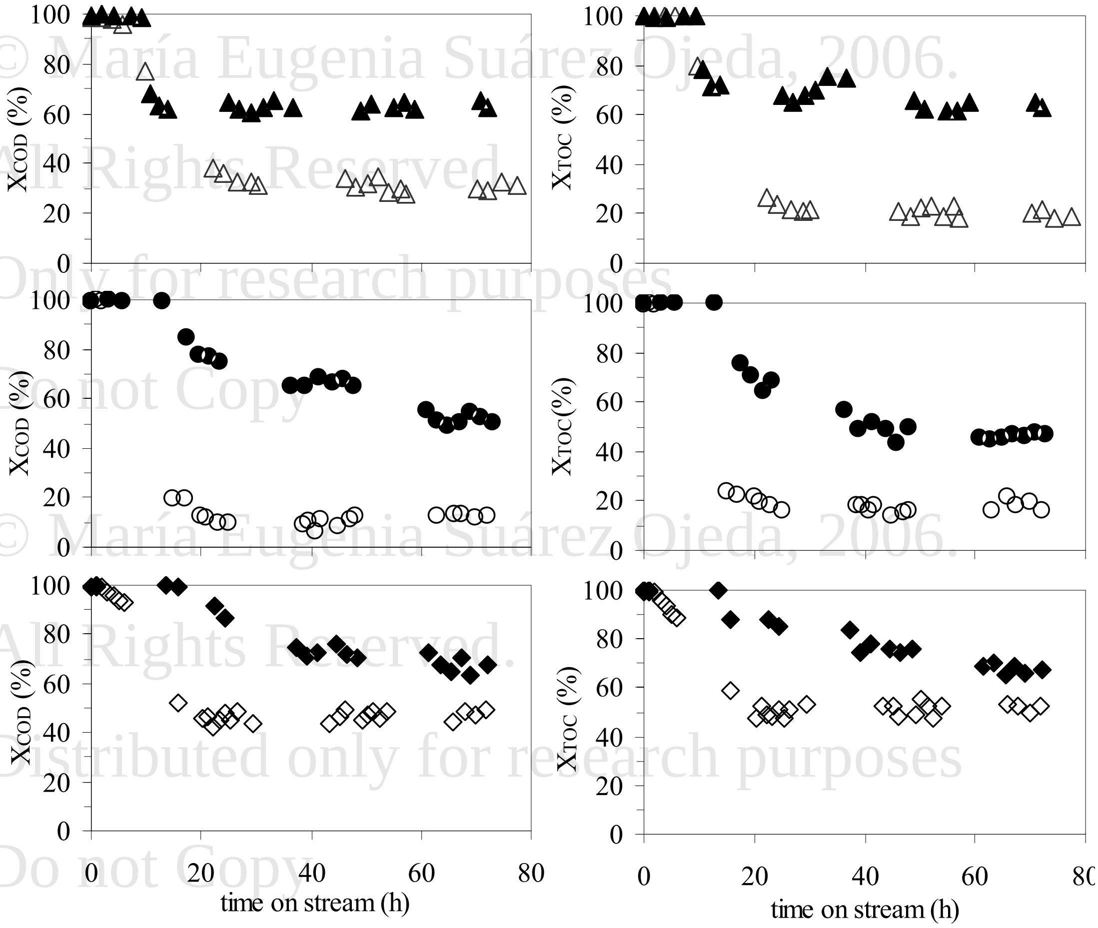

Figure IV.18. X_{COD} and X_{TOC} profiles at 2 bar for a) phenol, b) o-cresol and c) 2-chlorophenol. Empty symbols indicate CWAO test at 140ºC, filled symbols indicate CWAO tests at 160ºC.

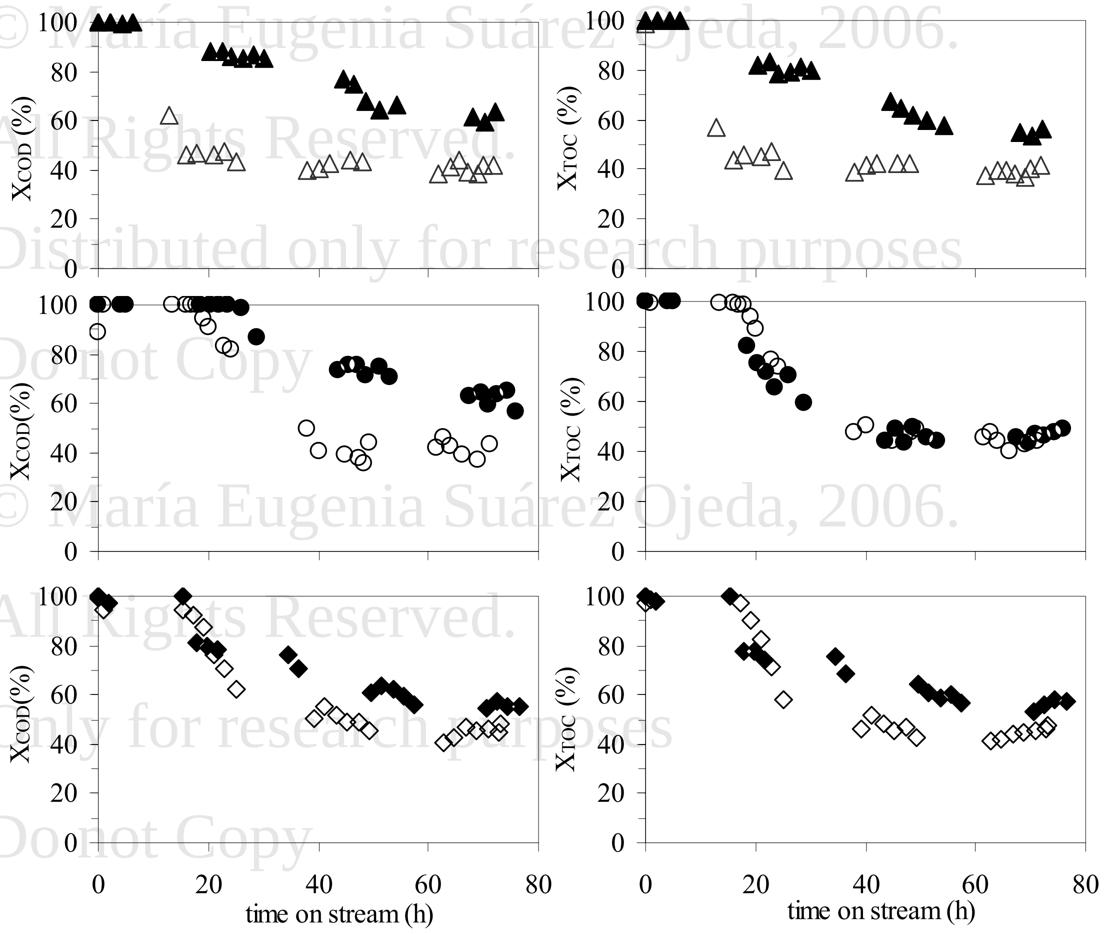

Figure IV.19. X_{COD} and X_{TOC} profiles at 9 bar for a) phenol, b) o-cresol and c) 2-chlorophenol. Empty symbols indicate CWAO test at 140ºC, filled symbols indicate CWAO tests at 160ºC.

The conversions (X, X_{COD} and X_{TOC}) at the end of the CWAO experiments are listed in Table IV.14. As expected, temperature has a strong influence on the conversions. For *o*-cresol, at 2 bar, X goes from 30% to 83%, X_{COD} from 12% to 53% and X_{TOC} from 8% to 47% as temperature increases from 140 to 160ºC. In turn, P_{O2} has a weaker effect on the overall conversions. For *o*-cresol, at 160ºC, X goes from 83% to 90%, X_{COD} from 53 to 66% and X_{TOC} from 46% to 47% as pressure increases from 2 to 9 bar. The same trends are found for the other compounds. However, a detailed inspection of Table IV.14, leads to an exception in the effect of P_{O2}, for o-cresol at 140ºC, a change in P_{O2} from 2 to 9 bar makes X to change from 33 to 97%. This unexpected result has no clear explanation and could be related to the changes in the AC catalytic activity by mass loss or AC pore blockage (thus low conversion at 140-2) or to the differences into the intermediates distribution, i. e. if the intermediates generated at 140-9 are of low reactivity, thus all the oxygen is available for o-cresol mineralization (high conversion at 140-9). Those factors will be discussed later on.

Table IV.14. Final conversions for CWAO tests.

		140ºC			160ºC		
Compound	P_{O2}	X(%)	X_{COD}(%)	X_{TOC} (%)	X(%)	X_{COD}(%)	X_{TOC} (%)
phenol	9 bar	58	42	32	80	58	52
	2 bar	45	33	21	78	65	62
o-cresol	9 bar	97	42	40	90	64	46
	2 bar	33	15	14	83	53	47
2-chlorophenol	9 bar	60	51	49	80	58	56
	2 bar	55	48	47	75	70	69

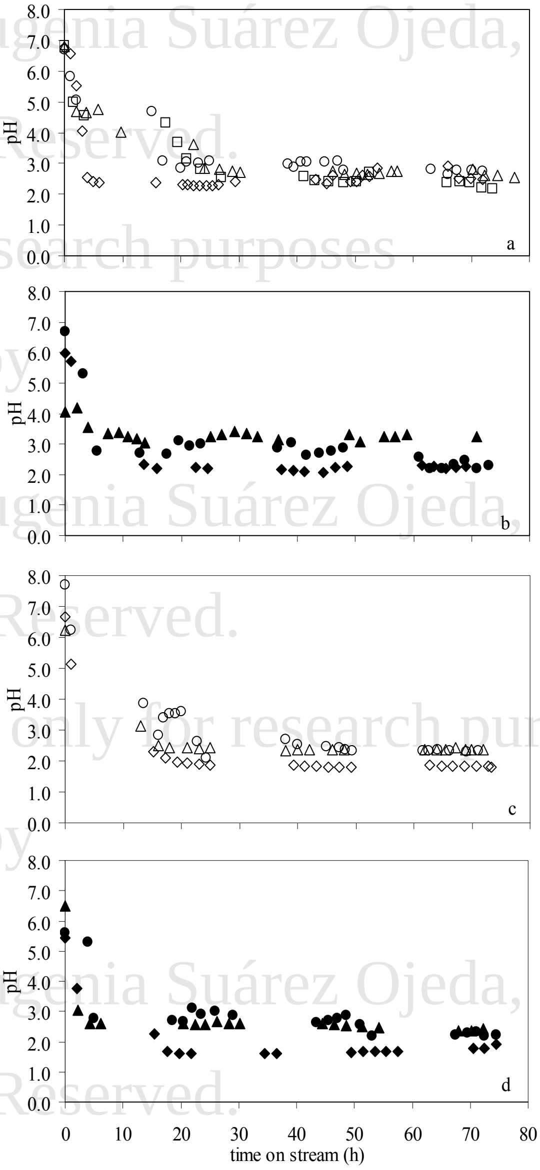

Figure IV.20. pH profiles for CWAO test at 2 bar of oxygen partial pressure a) for 140ºC and b) for 160ºC. pH profiles for CWAO test at 9 bar of oxygen partial pressure c) for 140 and d) for 160ºC. Open symbols refers to 140ºC and full symbols to 160ºC.

Obviously, X_{COD} is lower than the respective X because of the presence of partially oxidised products. It should be pointed out that the higher the difference between X and X_{COD}, the higher the amount of partially oxidised products in the liquid effluent. For example, the differences in the 140-2 tests are 18% for *o*-cresol, 15% for phenol and only about 7% for 2-chlorophenol. This demonstrates that 2-chlorophenol undergoes deeper oxidation towards carbon dioxide than phenol or *o*-cresol. The difference between X and X_{TOC}, which gives the selectivity towards carbon dioxide, could also confirm this. The carbon dioxide selectivity increases as X and X_{TOC} get closer. Hence, in 140-2 test, the differences were 9% for 2-chlorophenol, 17% for *o*-cresol and 24% for phenol. These values indicated that complete mineralization pathway also depends on the substituent involved, thus 2-chlorophenol seems to form intermediates more easily to oxidise.

As far as X is concerned, for CWAO tests performed at 140-2, the reactivity order (Table IV.14) is 2-chlorophenol > phenol > *o*-cresol, whereas in the case of 140-9 tests the following reactivity order is *o*-cresol > 2-chlorophenol ≈ phenol. For 160-2 the reactivity order was *o*-cresol > phenol ≈ 2-chlorophenol. Finally for 160-9 test, the reactivity order is *o*-cresol > 2-chlorophenol > phenol. However, it must be noticed for 9 bar test (Figure IV.16 and Figure IV.17) that the steady state is not clearly achieved (with the exception of phenol 140-9 test). This can be caused by a continuous loss in the AC weight due to side reactions as will be discussed later, which cannot be prevented at these severe conditions. Also, this loss in AC weight could explain the decrease in X observed for *o*-cresol test at 160-9 compared to the X at 140-9.

From these results it seemed that two different reaction mechanisms exist, mainly depending on the severity used in the CWAO test. At 140-9 and at 160ºC (both P_{O2}), it seems to follow an electrophilic substitution of the aromatic ring whereas at 140-2 it appeared to be a nucleophilic substitution of the aromatic ring [94].

In the nucleophilic aromatic substitution mechanism, the substituents can be classified by their capacity to stabilise the benzonium carbanion. The substituent is strongly deactivating if it withdraws electrons and strongly activating if it releases electrons. Hence, the chloride group (–Cl) is strongly activating and the hydroxyl and methyl, groups (-OH and $-CH_3$) are deactivating (in that order) for the nucleophilic aromatic substitution. Therefore, these compounds are expected to be eliminated in the order 2-chlorophenol > phenol > *o*-cresol, which match with the experimental results at 140-2.

De et al. [114] proposed this mechanism for the oxidation of phenol and 2-chlorophenol with hydrogen peroxide. The system studied was very similar to that of the present case because at the selected temperature AC could generate oxygen species similar to those occurring in the oxidation with hydrogen peroxide or ozone. Regardless the reactive species involved in the oxidation, the addition rate to the aromatic ring depends on the stabilisation of the benzonium anion. Therefore, the hypothesis that a nucleophilic aromatic substitution could be the reaction mechanism seems to be a reasonable explanation for the reactivity order found at 140-2.

For an electrophilic aromatic substitution, the mechanism passes through the benzenium cation or a sigma complex, so compared to the nucleophilic aromatic substitution, the substituent give an opposite effect. In this way, the activating groups in the nucleophilic substitution should help to refuse the electrophilic substitution in the aromatic ring. Hence, the compounds are expected to be destroyed in the order *o*-cresol > phenol > 2-chlorophenol, which matched closely the experimental results at 160-2 and at 9 bar both temperatures.

In the present conditions, the AC could be envisaged as a promoter in the generation of oxygen radicals similar to those coming from hydrogen peroxide and ozone. Therefore, it is possible that the molecular oxygen to subsequently form anions and radicals, which respectively behaves as nucleophiles and electrophiles in the reaction media. Regardless the reactive species involved in the oxidation, the addition rate of a nucleophile or an electrophile to the aromatic ring depends on the stabilisation of the benzonium carbanion or the sigma complex, respectively. Therefore, seems to be reasonable the hypothesis that a nucleophilic or an electrophilic aromatic substitution could be the first step in the reaction mechanism. However, the reactivity order is only a qualitative statement and the different steady state reactivity orders above listed could be largely affected by the temperature (activation energy effect), changes in the AC performance, as later discussed, competition with the other organic compounds for the available oxygen radicals, and even adsorption over the AC surface.

Regarding to the reaction intermediates, they were quantified by means of external standards. Later, using the obtained HPLC concentration, the theoretical oxygen demand (ThOD) of each one was calculated using the empirical correlations, based on the stoichiometric oxidation obtained by Baker et al. [119]. The partial oxidation products have been grouped into carboxylic acids, quinone-like products, condensation products and non-identified products. Later, the contribution of each group was compared to the total experimental COD obtained in each CWAO test. The results are summarised in Figure IV.21a, Figure IV.21b and Figure IV.21c, for phenol, *o*-cresol and 2-chlorophenol, correspondingly. It must be noted that besides a higher target conversion, a high selectivity towards carboxylic acids is desired, as they are usually more biodegradable.

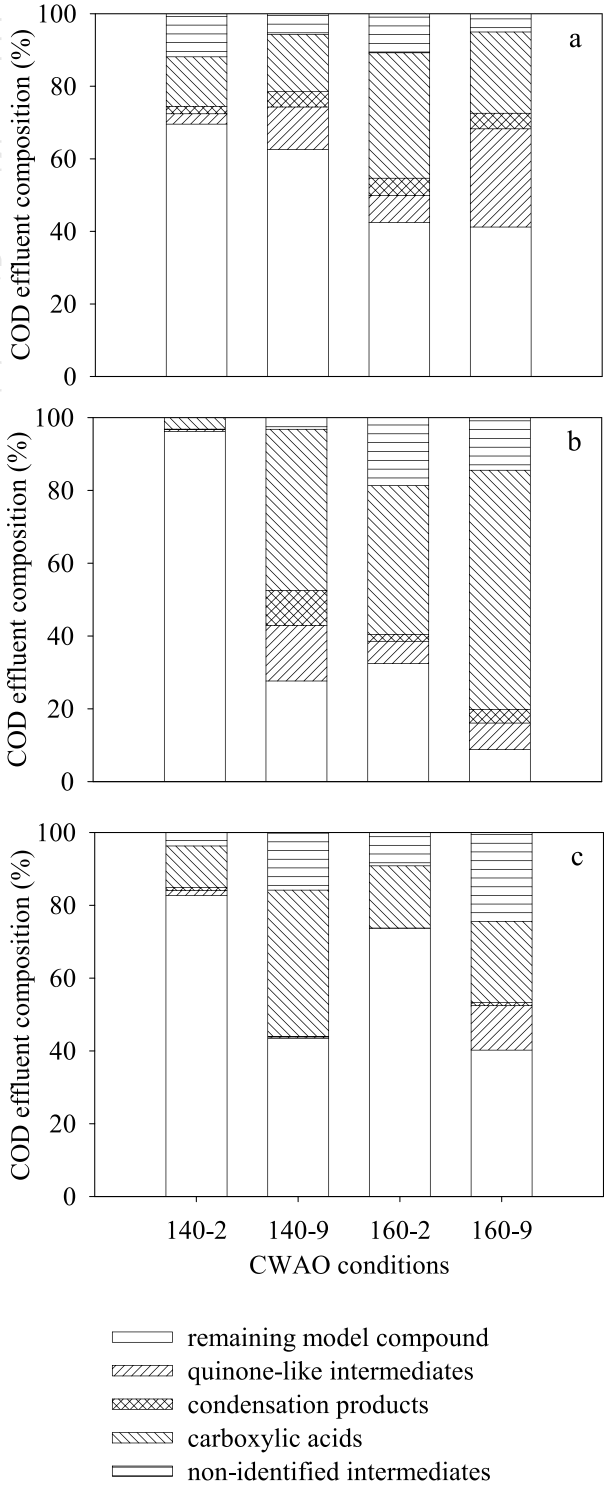

Figure IV.21. Intermediates distribution for phenol (a), *o*-cresol (b) and 2-chlorophenol (c) CWAO effluents.

From Figure IV.21a for phenol tests, the carboxylic acids fraction roughly increased, with the severity of the CWAO, however at 160-9 this fraction is lower than at 160-2. On the contrary, the quinone-like fraction behaviour was opposite to the carboxylic acids, demonstrating that the most severe condition (160-9) does not mean a real progression into the reaction pathway. At 160-2, the majority of the remaining COD was in form of phenol (42.5%) and carboxylic acids (34.6%); the rest was in form of quinone-like products (7.4%), condensation products (4.8%) and non-identified COD (10.8%). Formic, acetic and propionic acids were 87% of the COD in form of carboxylic acids, whereas *p*-benzoquinone and catechol were 81% of the COD in form of quinone-like products.

At 160-9, most of the remaining COD was in the form of phenol (41.2%) and quinone-like products (24%); *p*-benzoquinone and catechol were the 81% of the COD in form of quinone-like products, whereas the remaining COD is formed by carboxylic acids, about 22.4%, and mainly composed of acetic, maleic, succinic and 4-HB acids; these acids accounts for 89% of the COD in form of carboxylic acids.

At 140ºC most of the residual COD was in form of phenol, 69.5% and 62.5% at 2 bar and 9 bar of P_{O2}, respectively. The COD in form of carboxylic acids was 13.7% and 15.7% at 2 bar and 9 bar of P_{O2}, correspondingly, and it was composed mainly by acetic and propionic acid, being 95% (2 bar) and 51% (9 bar) of the remaining COD in form of carboxylic acids. The quinone-like products were mainly catechol for both P_{O2}, being its concentration always double than the concentration of hydroquinone and *p*-benzoquinone together.

From these results of phenol CWAO at 160-2, the reaction seems to evolve enough to oxidise most of the organic matter to formic, acetic and propionic acids, which are the latest intermediates before total mineralisation. However, at 160-9, the acids are of high molecular weight and the quinone-like products are in higher proportion, indicating that the reaction conditions were not severe enough, probably because there is not enough oxygen to perform both phenol oxidation and AC side reactions which prevents the phenol reaction from progressing. Similar trends can be withdrawn for 140ºC and both P_{O2}, although, in this case the reaction conditions were not sufficient to transform phenol into more oxidised intermediates.

For *o*-cresol, the intermediates salicylaldehide, 1-indanone, 1,3-benzodioxole and 2,2'-biphenol were included in Figure IV.21b as condensation products. As it can be seen, the remaining *o*-cresol decreased as the severity in the CWAO increased. However, it must be noticed that the *o*-cresol and carboxylic acids proportions were almost the same for 140-9 and 160-2, whereas, the lowest quantity of *o*-cresol and the highest amount of carboxylic acids occurred at 160-9. On the other hand, the condensation and quinone-like products show a maximum at 140-9, then diminish at 160-2 and remains almost constant at 160-9. At 160-9, most of the remaining COD was in form of carboxylic acids (65.7%) and it was composed mainly of glyoxilic, acetic and propanoic acids which represents the 94% of the COD in form of carboxylic acids. However, it must be noted that acetic acid concentration was three times higher than the concentration of glyoxilic and propanonic acid together. On the other hand, quinone-like products were composed mainly of catechol, hydroquinone and resorcinol, whereas *p*-benzoquinone was just present in trace amounts. At 140-9 and 160-2, which presents similar composition (Figure IV.21b), the residual COD was mainly in form of *o*-cresol, 27.6% (140-9) and 32.4% (160-2), and carboxylic acids, 44.3% (140-9) and 40.9% (160-2). The COD from carboxylic acids was again composed mainly of glyoxilic, acetic and propionic acids, being the 81% (140-9) and 92% (160-2) of the remaining COD in form of carboxylic acids. The quinone-like products were catechol and hydroquinone in the case of 140-9 whereas for those at 160-2, resorcinol was also present. The catechol concentration was always two to three times the concentration of the rest of quinone-like products. At 140-2, the residual COD was in form of *o*-cresol representing the 96.2% of the total COD. Again, most of the detected carboxylic acids were glyoxilic, acetic and propionic acids. The quinone-like fraction was exclusively formed by catechol.

Overall for *o*-cresol CWAO, at 160-9, the oxidation seems to be deep enough to convert most of the substrate to glyoxilic, acetic and propionic acids which are the latest intermediates before total mineralisation. At 140-9 and 160-2, the products distribution are similar, indicating that these reaction conditions were severe enough to oxidise the *o*-cresol but not sufficient to produce significant changes in the selectivity of the reaction towards carboxylic acids. For 140-2 bar, the reaction conditions were not sufficient to transform *o*-cresol into more oxidised intermediates. Note that glyoxilic acid and resorcinol were not detected during phenol CWAO, so the presence of these compounds suggests a different reaction pathway between phenol and *o*-cresol.

Finally, for 2-chlorophenol, from Figure IV.21c, it can be confirmed that 2-chlorophenol undergoes a higher degree of mineralisation, since the intermediates occurrence was lower than for the previous compounds. The remaining 2-chlorophenol lies between 85% of the identified COD (at 140-2 and at 160-2) and 40% of the identified COD (at 140-9 and at 160-9). Moreover, the carboxylic acids had the highest proportion in the remaining COD at 140-9 and 160-9, but again at the more severe condition the amount of quinone-like products was the highest, demonstrating that the most severe conditions did not guarantee an appropriate progression in the reaction. Probably what is happening is that AC side reactions compete with 2-chlorophenol oxidation at similar rate and there is not enough oxygen to perform both reactions which prevents the 2-chlorophenol oxidation from progressing. For this compound, the reaction condition at 140-9 looks to be the best condition toward acids selectivity. At 140-9, acids are the 40.1% of the total remaining COD, being formic, propionic and t,t-muconic acid 85% of the COD in the carboxylic acids fraction.

IV.3.2. AC Performance

The AC characterisation presented in this section takes into account the changes in weight and in textural properties suffered by the AC at the end of the CWAO tests. During the CWAO tests, the AC is suffering, at the same time, two processes: burning/oxidation and oxidative coupling reactions.

The M_{AC} (dried at 400ºC) will serve to quantify which process occurred in higher degree compared to the other: a positive M_{AC} means that oxidative coupling is higher or faster than burning/oxidation, whereas a negative M_{AC} means the reverse.

The TWL (Total Weight Loss, from TGA up to 900ºC) will serve to establish the degree of oxidative coupling reactions over the AC: the higher the TWL, the higher the development of oxidative coupling reactions are.

Finally, when the weight changes do not permit to distinguish which process of those occurring over the AC are the dominating one, the textural properties (surface area, micropore volume and macro and mesopores cumulative area surface) will serve to clarify the situation.

As Table IV.15 and Table IV.16 show, M_{AC} was either positive (i. e. the AC weight increased) or negative depending on the compound and the operating conditions. In the less severe CWAO conditions (at 140-2), the M_{AC} was positive. Then, at 140-9 and 160-2, the M_{AC} is positive for phenol and *o*-cresol whereas for 2-chlorophenol it was negative. Finally for the most severe oxidative condition (at 160-9) the M_{AC} was always negative. M_{AC} had been previously studied for phenol CWAO, at 140-9 [48, 57]. In these studies, it was observed that, from the starting up, the AC weight first underwent an increase, then reached a maximum and later decreased to values far below the original weight, resulting in a catalyst loss by direct AC oxidation/burning, 33% after 96 h at the reported conditions. The early increase was due to the irreversible deposition of phenolic polymers by oxidative coupling. AC oxidation was the responsible of the subsequent decrease. When the P_{O2} was decreased to 2 bar, the AC weight always increased.

Table IV.15. Original bed loading, M_{AC} and textural characterization at the end of CWAO tests at 140ºC.

Compound	P_{O2}	M_{AC}(%)	BET surface Area (m^2 g^{-1})	Micropore Volume (cm^3 g^{-1})	BJH cumulative surface area (m^2 g^{-1})
Original AC	-	-	1481	0.343	304
phenol	9 bar	3.6	284	0.003	191
	2 bar	7.1	122	0.003	96
o-cresol	9 bar	19.3	122	0.002	75
	2 bar	17.0	24	0.001	2
2-chlorophenol	9 bar	-38.9	201	0.008	148
	2 bar	26.2	169	0.002	120

Table IV.16. Original bed loading, M_{AC} and textural characterization at the end of CWAO tests at 160ºC.

Compound	P_{O2}	M_{AC}(%)	BET surface Area (m^2 g^{-1})	Micropore Volume (cm^3 g^{-1})	BJH cumulative surface area (m^2 g^{-1})
Original AC	-	-	1481	0.343	304
phenol	9 bar	-57.4	280	0.003	253
	2 bar	7.4	243	0.007	131
o-cresol	9 bar	-62.3	109	0.004	83
	2 bar	54.2	77	0.003	52
2-chlorophenol	9 bar	-52.6	260	0.006	153
	2 bar	-16.5	474	0.004	315

Many studies [103-105] have shown that this increase in AC weight could be attributed to the deposition of polymeric compounds produced by oxidative coupling reactions over the AC. Cooney and Xi [90] demonstrated that, at low pHs, oxidative coupling reactions can be accelerated by the presence of a substituent on the phenol molecule. They postulated that oxidative coupling reactions simultaneously occur with the oxidation reaction and these coupling reactions probably block either the active sites or the pores in AC, thus decreasing its catalytic activity. According to Cooney and Xi [90], oxidative coupling reactions follow the order o-cresol > 2-chlorophenol > phenol. However, for 140-2, where AC oxidation should be less important, the observed order in M_{AC} is 2-chlorophenol > o-cresol > phenol, which differs from that predicted. In any case, the occurrence of oxidative coupling could affect the subsequent AC performance.

TGA were performed to find out which kind of compounds could be responsible for the weight change and to evaluate the amount of adsorbed products. Figure IV.22 show the thermograms and their first derivatives (dW/dT) for each AC used in the CWAO tests, during the TGA performed between 100 and 900ºC under nitrogen flow.

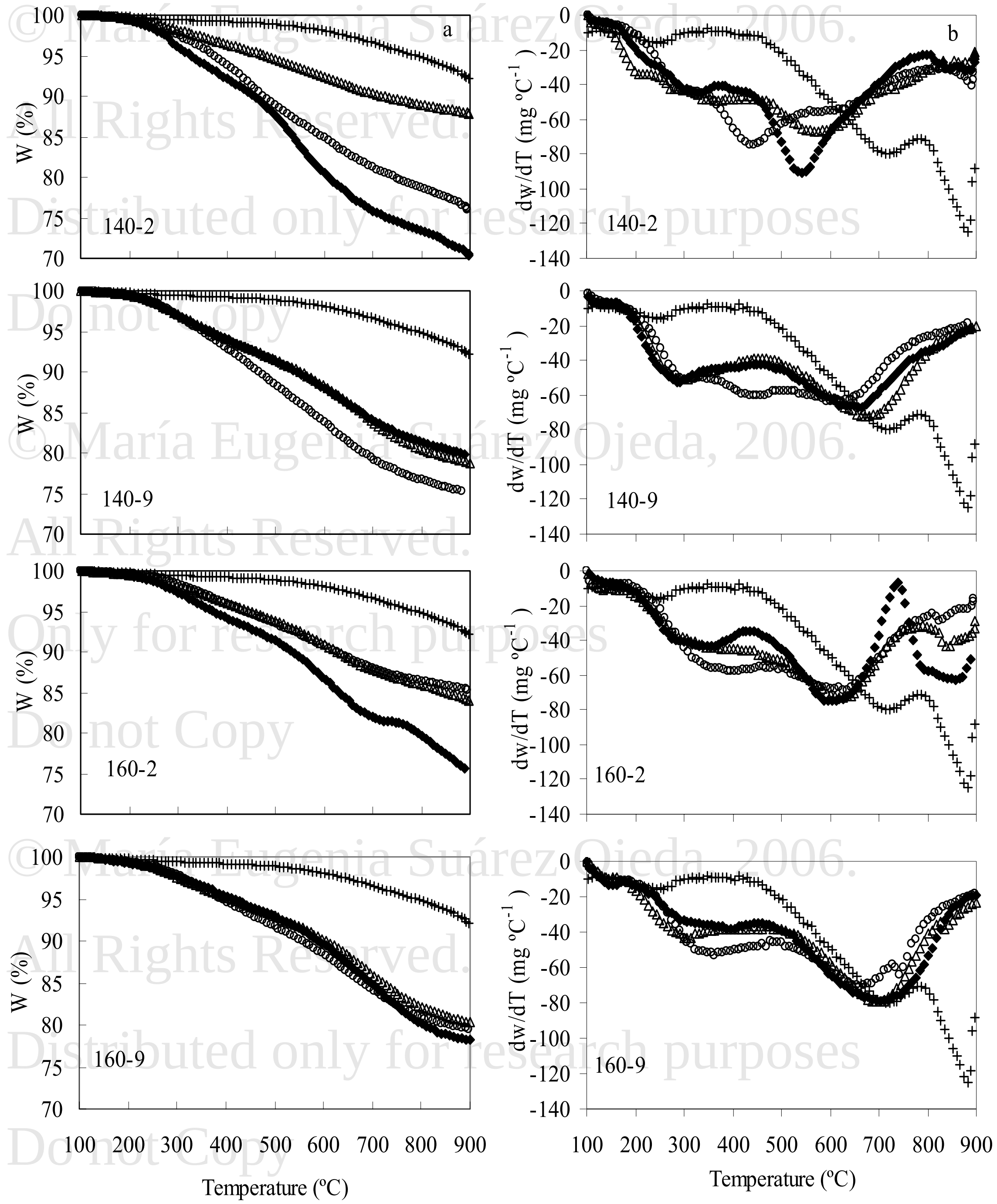

Figure IV.22. TGA profiles (a) and first derivative of TGA profiles (b) of original and used AC after being tested in 72 h CWAO experiments. CWAO temperature and pressure are shown in each graph. {(+) virgin AC, (♦) 2-chlorophenol, (Δ) phenol, and (○) *o*-cresol}

According to Figueiredo et al. [106], the surface species attached to an AC are desorbed at different temperatures. Thus, from 100ºC to 300ºC, the slow release of species is assumed to be related to the decomposition of carboxylic groups into CO_2. Meanwhile, the zone between 300ºC and 900ºC can be assigned to the release of CO_2 due to the decomposition of lactones and CO from oxygen surface groups such as carboxyl, phenyl and ethyl groups.

In the case of used AC in CWAO tests, the weight loss in the first zone between 100 to 300ºC should also include the release of physisorbed model compounds and reaction intermediates, whereas beyond 300ºC, in the second zone, must include the decomposition of chemisorbed species, including the cracking of polymers from oxidative coupling reactions. From Figure IV.22b, the dw/dT of the AC used at 140-2 shows a maximum peak in the zone of chemisorbed species release. For the AC used at 140-9, 160-2 and 160-9, the dw/dT presents not only a peak in the second zone but also a second maximum peak developed in the first zone of rapid release of physisorbed compounds. However the peaks of the first zone in the TGA fron used AC at 160-9 are more developed thatn in the others ACs.

Turning to TWL results, at 140-2, from Table IV.15 in the case of phenol test, the TWL is the smallest but the M_{AC} is a slightly higher than at 140-9 which could indicates that both processes were occurring at the same proportion (M_{AC} are similar), but being oxidative coupling a little bit slower than AC oxidation/burning (TWL is12% at 140-2 but 21% at 140-9). For o-cresol and 2-chlorophenol (at 140-2) the rate of oxidative coupling seems to be higher than in the case of phenol since the TWL are between 24 and 30 % (Table IV.15). From the textural characterisation, the AC used in o-cresol test at 140-2 display the highest surface area loss (BET surface area of 24 $m^2\ g^{-1}$ and BJH cumulative area surface of 2 $m^2\ g^{-1}$) therefore, is confirmed that oxidative coupling reactions occurs in a higher degree than AC burning/oxidation.

On the contrary, for the test at 140-9, the AC used in the phenol CWAO approaches its behaviour to the other ACs used in o-cresol and 2-chlorophenol 140-9 tests, therefore, for phenol, the oxidative coupling reactions seems to predominate in front of AC oxidation/burning at 140-9 in despite of being the M_{AC} of phenol at 140-9 the smaller compared to the M_{AC} of o-cresol and 2-chlorophenol at 140-9. However, when checking the textural characterisation, the AC used for phenol test at 140-9 has a surface area loss (284 $m^2\ g^{-1}$ of BET surface area and 191 $m^2\ g^{-1}$ of BJH cumulative area surface) smaller than the presented by the AC used in o-cresol (122 $m^2\ g^{-1}$ of BET surface area and 75 $m^2\ g^{-1}$ of BJH cumulative area surface) and 2-chlorophenol (201 $m^2\ g^{-1}$ of BET surface area and 148 $m^2\ g^{-1}$ of BJH cumulative area surface) tests; consequently, for phenol, oxidative coupling cannot be higher than AC burning/oxidation.

From Table IV.16, at 160-2, the ACs used for phenol and o-cresol tests again behaves in a similar manner, its TWL are more or less 16 %, whereas for 2-chlorophenol the TWL is

25%. These results seem to indicate for phenol and o-cresol that oxidative coupling reactions could be faster than AC oxidation/burning. However for 2-chlorophenol the TWL is similar to the ACs used at 140-2 and 140-9 (25 and 30%, respectively), so oxidative coupling reactions seem to be equally important than AC oxidation/burning in despite of being the M_{AC} positive or negative. It must be noticed the unexpectedly high positive M_{AC} obtained for o-cresol at 160-2, which agrees with the low BET surface area but disagrees with the TWL measured. No evident explanation exists for this value, although it could be speculated that oxidative coupling early occurred into the pores entrance, mostly blocking their availability for subsequent adsorption. As it can be seen in Table IV.16, the micropore volume after use is almost negligible when compared to that original. On the other hand, the AC used in the 2-chlorophenol test at 160-2 show the highest surface area preservation (474 m^2 g^{-1} of BET surface area and 315 m^2 g^{-1} of BJH cumulative area surface), so, in spite of being the oxidative coupling reactions considerable high (25% of TWL), the AC burning/oxidation took place in a degree which permitted to quickly burn/oxidise the polymers from oxidative coupling without loosing to much AC.

Finally, from Table IV.16, at 160-9, the ACs used in all the cases show the same behaviour and its TWL lies between 20 and 22%. These results together with M_{AC} (Table IV.16) show that the AC oxidation/burning (M_{AC} are always negative) could be greater than oxidative coupling reactions. This statement is confirmed by the textural characterisation, in spite of loosing the AC by burning/oxidation, the surface area preservation (Table IV.16) indicates that polymers of oxidative coupling were burned/oxidised at the same time or faster than the original AC.

The textural properties (Table IV.15 and Table IV.16) also changed according to the compound and the operating conditions. The lowest surface area and micropore volume seems to correspond to the less severe CWAO condition (140-2), regardless the model compounds considered. On the other hand, for the rest of conditions, the textural properties vary with each compound and CWAO conditions, as example, the maximum in micropore volume occurs for phenol at 160-2, for o-cresol at 160-9 and for 2-chlorophenol at 140-9. Although the microporosity is almost eliminated after the AC use in the CWAO tests, it seems that a maximum in the remaining microporosity, which also should correlate with mesopore availability, corresponds to a higher progression in the oxidation reaction for all model compounds and vice versa. In fact, from Figure IV.21, the maximum proportion of carboxylic acids occurred in the CWAO experiments at 160-2 for phenol, at 160-9 for *o*-cresol and at 140-9 for 2-chlorophenol, the same conditions of maximum microporosity, indicating that selectivity towards carboxylic acids could be related with keeping the microporosity in the AC or its active sites availability.

As demonstrated by the textural characterisation, a minimum loss in AC activity matches a maximum of CWAO development, since oxidative coupling blocks the active sites and AC oxidation/burning diminishes the surface area and, therefore, the catalytic activity. According to the present results, all the side-reactions must be taken into account to explain the reactivity order found and the CWAO deepness in each test.

IV. 4. Acknowledgements

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CHAPTER V. BIODEGRADABILITY ENHANCEMENT, INTERMEDIATES INFLUENCE AND FEASIBILITY OF COMBINED TREATMENT.

Some parts of the material appearing in this chapter have been used to write the article: Suárez-Ojeda, M. E.; Guisasola, A.; Baeza, J.A.; Fabregat, A.; Stüber, F.; Fortuny, A.; Font, J. and Carrera, J. Integrated catalytic wet air oxidation and aerobic biological treatment in a municipal WWTP of a high-strength o-cresol wastewater. Submitted to Chemosphere. May 2006.

Outlook

This chapter examines the biodegradability, toxicity and inhibition of the effluents coming from catalytic wet air oxidation (CWAO) of phenol, 2-chlorophenol and *o*-cresol. The main goal is to find the optimal conditions (in terms of temperature, pressure, catalyst performance and biodegradation parameters) for the oxidation step, so that these effluents can be successfully treated in a municipal wastewater treatment plant (WWTP) as a part of the influent of a municipal WWTP. As explained in Chapter IV, twelve CWAO experiments using activated carbon (AC) as catalyst were conducted for phenol, *o*-cresol and 2-chlorophenol. In this Chapter, respirometric experiments were completed before and after each CWAO experiment using a conventional activated sludge coming from a municipal WWTP. The biodegradation parameters (i.e. maximum Oxygen Uptake Rate (OUR_{max}) and Oxygen Consumption (OC) were calculated in each respirometry. Moreover, the biodegradability of the intermediates was examined and they were classified in readily biodegradable, inert or toxic/inhibitory compounds. The heterotrophic yield coefficient (Y_H) was obtained for the readily biodegradable compounds. The biodegradation parameters for inert compounds were obtained at one concentration whereas these parameters for toxic/inhibitory compounds were obtained at two different concentrations. These data allow to understand the biodegradability of each CWAO effluent and to establish the optimal conditions in the oxidative step for this kind of phenolic compounds.

This detailed study allows achieving a successful coupling of CWAO–aerobic oxidation for the treatment of a model wastewater containing phenol and o-cresol in pilot scale. The original wastewater was non-readily biodegradable and has an inhibitory effect over non-acclimatised activated sludge; however, using a proportion of 30% of CWAO effluents in the inlet to the pilot plant, the integrated CWAO-biological treatment achieved a 98% of total COD removal and, particularly, a 91% of CWAO effluent COD removal without any undesirable effects on the biomass.

V. 1. Introduction

Phenolic compounds are considered as prior pollutants because of its effect on humans (e.g. teratogenic, mutagenic, carcinogenic or toxic) and on the environment. The introduction of these compounds into the environment during the last few decades has given rise to major concern about the ecotoxicological effects and ultimate fate of these compounds.

Biological treatment of this kind of compounds is usually not straightforward. On the one hand, there is low removal efficiency. Moreover, these compounds can be toxic for a biological treatment. For instance, the EC_{50} values for some phenolic compounds are: 30.1 mg l^{-1} for phenol [110], 5.0 mg l^{-1} for *o*-cresol [110] and 2.6 mg l^{-1} for 2-chlorophenol [111] in microbial toxicity studies with *Daphnia Magna* exposed for 48 hours.

On the other hand, chemical oxidation methods aiming a complete destruction might become extremely cost-intensive. In fact, Marco et al. [39] said that investment cost for biological processes may range from 5 to 20 times less than those of chemical processes such as ozonation or hydrogen peroxide oxidation.

Often, a combination of two or more treatments can solve these pollution problems in a cost-competitive way, so a coupling of an initial oxidative step followed by biological treatment is a promising idea as demonstrated by the great effort invested into such integrated process over the last 15-20 years [72, 129].

The type of chemical pre-oxidation used in integrated processes is highly dependent on the characteristics and nature of the wastewater to be treated [123]. Wet Air Oxidation (WAO) would be a suitable technique for effluents having a Chemical Oxygen Demand (COD) loads from 10 to 100 g l^{-1} and the use of a catalyst would allow to decrease the temperature and pressures by 50ºC and 40 bar, respectively, as suggested by Debellefontaine et al. [130]. Moreover, according to the review done by Stüber et al [131], Catalytic WAO (CWAO) yielded satisfactory results in laboratory scale studies at relatively mild operating conditions of temperature and pressure, which lead to substantially lower investment and operation cost. Finally, CWAO becomes especially attractive when coupled with a biological treatment, because avoids the need for complete mineralization, which is often difficult to achieve under CWAO reaction conditions.

Therefore, Catalytic Wet Air Oxidation (CWAO) is a methodology for dealing with those hazardous wastes that are not suitable to biological treatment. As summarised in Table V.17, several studies about the biodegrability, toxicity or inhibitory effects of CWAO effluents have been published [26, 120-128]. However, these studies consider neither the intermediates of the CWAO nor their effect upon the biological treatment.

Few works examine the relationship between the intermediates formed in the CWAO step and the following biodegradation step. For example, Santos et al. [132, 133] used the Microtox® EC_{50} values of the intermediates appeared in the oxidation of phenol to predict the toxicity of the CWAO effluent in its posterior biological oxidation. Thomsen and Kilen [134] studied the intermediates in the wet air oxidation of quinoline and their toxicity using a test of nitrification inhibition. Finally, Hsu et al. [135] showed that biodegradability (expressed as BOD_5/COD) of ozonised phenolic solutions was strongly dependent on the accumulation and type of intermediates.

The standard BOD test at 5 days (BOD_5) has been commonly employed as a measurement of aerobic biodegradability. This test is widely used to estimate organic water pollution and to control the performance of WWTPs. However, BOD_5 measurement is very questionable when the effluent contains toxic or inhibitory compounds, similar to those found in industrial effluents [136].

Besides from the classical BOD_5, the impact of toxic or inhibitory compounds on WWTPs can be assessed either by a chemical characterisation of the effluent before and after biodegradation, or by several toxicity screening procedures based on bacterial luminescence (Microtox® test), mobility of cells (*Daphnia magna*, etc), inhibition of enzymatic activity (dehydrogenase, ATP), inhibition of nitrification, metabolic heat production (microcalorimetry techniques) or the oxygen consumption rate measurements (respirometry).

Table V.17. Evolution of biological properties upon CWAO

Reference	Type of effluent	CWAO Conditions	Biological Test
[120]	Wastewater from alkaloid factory mainly morphine, aniline, and toluol	T, P, t =150ºC, 6.5 bar, 2 h. Batch reactor Catalyst: metal salts	BOD$_5$/COD ratio
[121]	2,4-dichlorophenol	T, P_{O2} = 180-240ºC, 15 bar. Upflow fixed bed reactor, catalyst: Mn/Ce heterogeneous.	BOD$_5$/COD ratio
[122]	1-Amino-8-napthol-3,6-disulfonic acid	T, P_{O2}, t = 180-220, 30 bar, 2 h. Batch reactor Catalyst: Cu/Zn, Ce/Cu, Cd/Ce/Cu, Co/Bi and Ce/Fe heterogeneous composites	BOD$_5$/COD ratio
[123]	Wastewater from green olives processing (diluted)	T, P, t = 170-210ºC, 30-70 bar, 6 h. Batch reactor Catalyst: Cu^{+2}	BOD evolution and BOD$_5$/COD ratio
[124]	Olive mill effluent (diluted)	T, P, t = 180ºC, 70 bar, 6 h. Batch reactor Catalyst: Platinum over γ-Alumina and CuO over active carbon.	BOD evolution and BOD$_{15}$/COD ratio
[125]	Wastewater from pulp and paper mill	T, P_{O2}, t = 130-200ºC, 10 bar, 2 h. Batch reactor Catalyst: Cu/Co/Bi-C, Co/Bi-C, Fe/Mn-C over alumina and active carbon.	BOD$_5$/COD ratio BOD$_5$/COD ratio
[126, 127]	Acid Orange II	T, P_{O2}, t = 180-240ºC, 10-30 bar, 2 h. Semi-batch reactor. Catalyst: $CuO/ZnO/Al_2O_3$	BOD$_5$/COD ratio
[26]	Sodium dodecylbenzene sulfonate (DBS)	T, P_{O2}, t = 180-240ºC, 15 bar, 2 h. Semi-batch reactor. Catalyst: H_3PO_4 (acid catalysis)	Monitoring of TOC, COD, optical cell density, intermediates and residual DBS after treatment in biological shake flask
[128]	Kraft bleach plant effluents	T, P = 190ºC, 55 bar. Trickle bed and batch-recycle reactors. Catalyst:TiO_2 and Ru/TiO_2	Daphnia Magna 48 h EC$_{50}$ and Microtox 30 min EC$_{50}$
[132, 133]	Phenol [132, 133], catechol and hydroquinone [132]	T, P_{O2}, t = 140ºC, 16 bar, 30-250 min. Batch reactor. Catalyst: Commercial Cu based	effluents and intermediates: Microtox 15 min EC$_{50}$

There is no consensus about which is the better ecotoxicological test to use [137]. Probably, Microtox® and respirometry are the most widespread techniques but some works comparing both tests concluded that respirometry is more representative because the toxicity is evaluated directly on the WWTP sludge. Microtox® determinations could give an overestimation of the toxicity since the bacteria used correspond to a single marine microbial species (*Vibrio fischeri*) whose habitat is very different to a WWTP [138, 139].

Therefore, respirometry seems to be the most adequate technique to assess biodegradability, toxic and inhibitory effects of certain compounds to a certain biomass because the activated sludge from municipal WWTP can be directly used. Some authors used respirometry to estimate the effects of phenolics compounds (phenol, catechol, resorcinol, toluene, benzene, *m*-cresol, 4-nitrophenol, 3,5-dichlorophenol, 4-chlorophenol and 2,4-dichlorophenoxyacetic) on different activated sludge [69, 70, 140-143].

The knowledge of the physical, chemical and biological properties of the major reaction intermediates are key points in the integration of chemical and biological processes for water treatment [72]. This study, divided in two parts, aims to design an integrated treatment of substituted phenols: CWAO followed by a classical biological treatment.

In the Chapter IV, the influence of oxygen partial pressure and temperature on continuous CWAO of three model compounds (phenol, *o*-cresol and 2-chlorophenol) was investigated. CWAO was carried out in a fixed bed reactor in trickle flow regime, using a commercial activated carbon (AC) as catalyst. The major reaction products identified were low-molecular carboxylic acids and quinone-like compounds. The substrate removal effectiveness and the occurrence of oxidative coupling reactions over the AC were established for each compound.

The aim of this chapter is to establish the relationship between biodegradability, toxic and inhibitory effects with the composition of the twelve CWAO effluents generated previously. The objective is to ensure a viable coupling of the CWAO effluents as a regular part of the influent to a municipal WWTP. The biodegradation parameters of the CWAO effluents were achieved by means of respirometry and related to the intermediates compounds (carboxylic acids and quinone-like products) identified in Chapter IV.

Also, to validate the systematic approach developed to select the better CWAO condition and to track the behaviour of microorganism in front of increasing loads of CWAO effluents in the total influent to the plant, the CWAO effluents coming from o-cresol treated at 160-2 had been coupled with an activated sludge pilot plant. These results will be discussed in detail at the end of the chapter. Finally, the adaptation of the biomass to the CWAO main intermediates after 120 days of continuous operation was established by respirometry.

V.2. Experimental

V.2.1. Experimental set-up for respirometry screening tests.

A respirometer is a small biological reactor for the measurement of biological oxygen uptake rate (OUR). The respirometer used in this work corresponds to a LFS type, in which dissolved oxygen concentration (S_O) is measured in the liquid-phase (L) which is static (S) and continuously aerated (F) [68].

The air flows through a pressure manoreductor and through a gas rotameter (AAlborg 150 mm with micro-regulation valve) to ensure constant airflow. The vessel (1 litre) is magnetically stirred to avoid dead zones in air diffusion. The pH, S_O and temperature are measured with pH and S_O probes (WTW Sentix 81 and Cellox 325) which are connected to a PC using a multiparametric module (WTW Inolab 3). The respirometer is submerged in a temperature bath, set at 31 ºC, and the pH is maintained at 7.5 ± 0.5.

The OUR profile is obtained by solving the oxygen mass balance in the liquid phase of the respirometer. The value of the oxygen transfer coefficient (k_La) is required and it is calculated following the procedure originally described by Bandyopadhyay et al. [144]. The S_O profile or respirogram depends on the experimental conditions and the type of respirometer. A typical LFS respirogram and its characteristic parameters are presented in Figure V.23.

The five characteristic parameters (or direct parameters) of the respirogram are the initial Peak Slope (PS), the Peak Height (PH), the equilibrium oxygen concentration (S_{OE}), the final oxygen level (S_{Ofin}) and the Peak Area (PA). A detailed description of these parameters can be found elsewhere [71, 145].

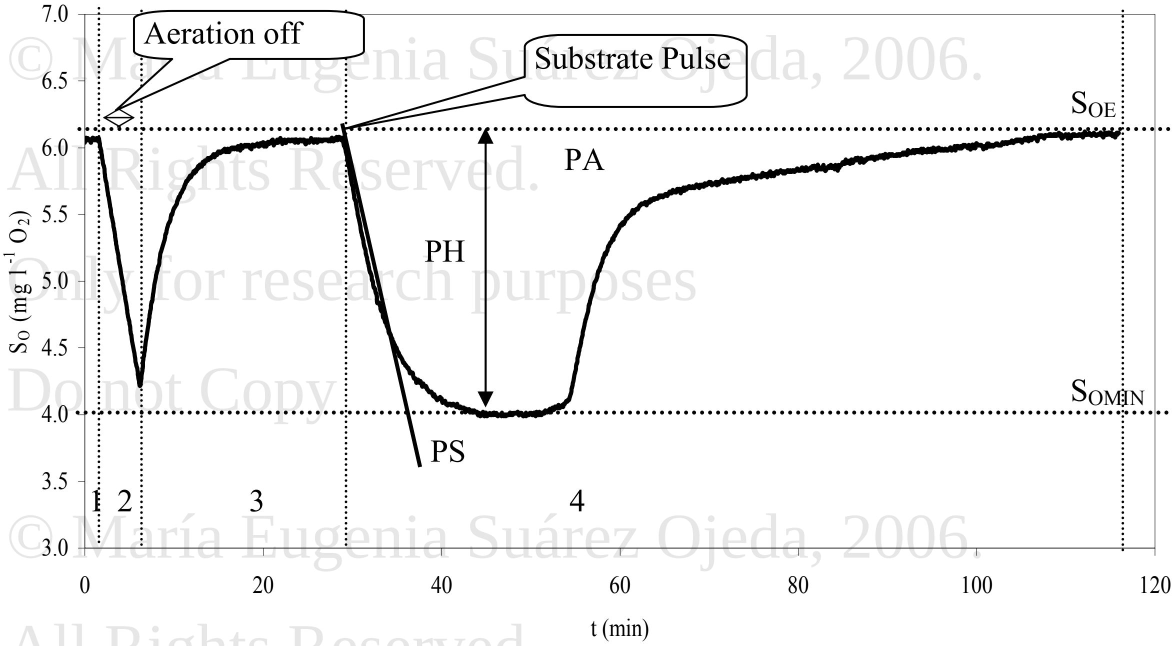

Figure V.23. Typical LFS Respirogram

In a continuously aerated respirometer, the dissolved oxygen (S_O) balance in the liquid phase of the reactor (Equation V.6) must be solved in order to obtain the oxygen uptake rate (OUR) profile:

$$\frac{d(S_O \cdot V_L)}{dt} = V_L \cdot k_L a \cdot \left[S_O^{\,*} - S_O(t)\right] - V_L \cdot OUR(t)$$ Equation V.6

If the volume of the liquid phase is assumed to be constant and the OUR is divided into endogenous (OUR_{END}) and exogenous (OUR_{EX}), the OUR profile due to the pulse of substrate can be expressed as:

$$OUR_{EX}(t) = k_L a \cdot \left[S_O^{\,*} - S_O(t)\right] - OUR_{END} - \frac{dS_O}{dt}$$ Equation V.7

Hence, three parameters are required to calculate the OUR_{EX} profile (k_La, OUR_{END} and S_O*). Experimental estimation of S_O* is a rather tedious process which can be avoided by handling numerically the oxygen balance. As can be observed in Figure V.23, the S_O remains constant at a certain value (S_{OE}) before the substrate pulse is added. This value (S_{OE}) balances the oxygen transferred due to the external aeration with the endogenous oxygen consumption. At this point, the S_O balance becomes:

$$\frac{dS_O}{dt} = 0 = k_L a \cdot \left[S_O{}^{*} - S_{OE}\right] - OUR_{END}$$

Equation V.8

Then, combining equations V.7 and V.8, equation V.9 is obtained which allows the OUR_{EX} profile evaluation from the respirogram.

$$OUR_{EX}(t) = k_L a \cdot \left[S_{OE} - S_O(t)\right] - \frac{dS_O}{dt}$$

Equation V.9

At this point, the only unknown parameters to solve the balance are k_La and S_{OE}, which are evaluated through a least-square optimisation process on the reaeration profile obtained with the action of turning the aeration on after having quantified the OUR_{END} value (Figure V.23). Reorganizing the equation V.6, the reaeration profile can be expressed as following:

$$\frac{1}{k_L a} \cdot \frac{dS_O}{dt} + S_O(t) = S_O * - \frac{OUR_{END}}{k_L a}$$

Equation V.10

Combining with equation V.10, equation 11 is obtained:

$$\frac{1}{k_L a} \cdot \frac{dS_O}{dt} + S_O(t) = S_{OE}$$

Equation V.11

The analytical solution of equation V.6 describes the S_O profile in the reaeration phase (Equation V.12). The k_La value is obtained by fitting the experimental reaeration profile with the theoretical profile (Equation V.11) using a least square method.

$$S_O(t) = (S_O(0) - S_{OE}) \cdot e^{(-k_L a \cdot t)} + S_{OE}$$

Equation V.12

A typical LFS respirogram (Figure V.23) starts with a decreasing S_O concentration because the aeration is stopped. This decrease is used to estimate the value of the OUR endogenous. Then, aeration is turned on and the S_O rises progressively up to the S_{OE} value. This reaeration profile is used to estimate the k_La and S_{OE} values. Once the S_{OE} level is reached, a pulse of substrate is added and the SO level drops sharply due to the OUR_{EX} (Equation V.13).

$$\frac{dS_O}{dt} = k_L a \cdot \left[S_O * - S_O(t)\right] - OUR_{END} - OUR_{EX}$$

Equation V.13

When the substrate is totally consumed, the S_O level returns to the original S_{OE} level, as the OUR value also returns to the endogenous value.

From the S_O profile by solving the mass balance in the liquid phase for the oxygen, the Oxygen Uptake Rate (OUR) profile (Figure V.24) is obtained as well as indirect parameters like maximum OUR (OUR_{MAX}) and total oxygen consumption (OC) that, combined with the direct parameters, serve to asses the toxicity and inhibition levels.

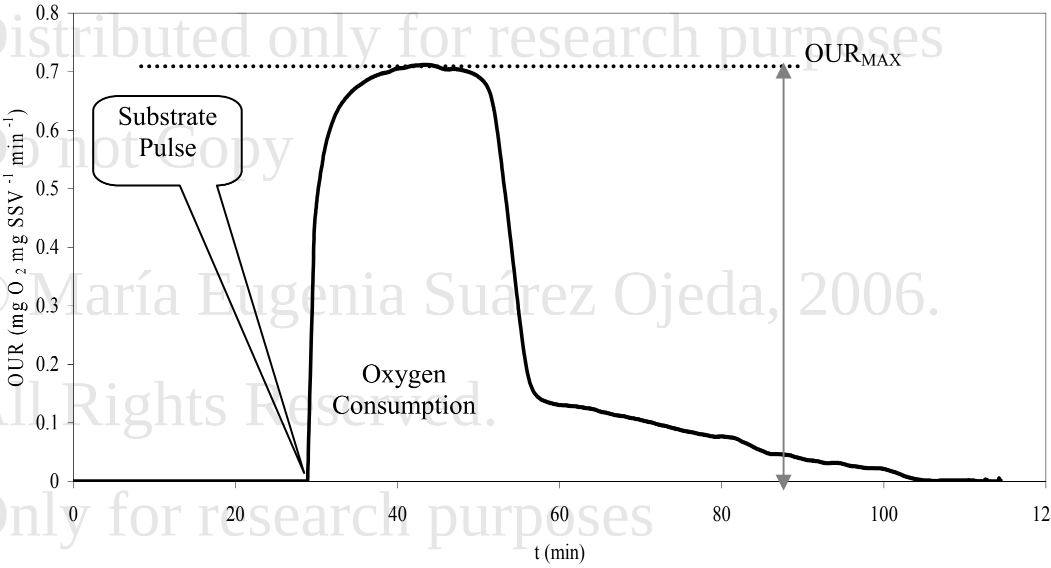

Figure V.24. Typical OUR profile from a LFS respirogram obtained with 50 mg COD l^{-1} of acetate

A program developed in MATLAB® 6.1 for data handling enables to calculate the OUR profile as a function of time (Figure V.24) and the biodegradation parameters described next. A respirometer picture could be found in Annex I.

V.2.2 Biodegradation Parameters Determination.

The procedure used in this study to determine the toxicity or inhibition level of a certain compound was proposed by Guisasola et al. [71]. They proposed a respirometric methodology valid even if the compound has a biodegradable fraction. Four respirometric tests are needed to assess the biodegradability, toxicity or inhibition level (biodegradation parameters) of a certain compound. The procedure of a respirometric experiment performed in this work is summarised next:

a) Run 1: A pulse of 20 mg COD $l^{-1}$of a control substrate (sodium acetate) is added in the first step.

b) Run 2: A pulse of the possible toxic/inhibitory compound (tested compound) is added in the second test, after the control substrate is consumed. The biodegradability of this compound can be assessed in this run.

c) Run 3: The third step is the addition of the same pulse of control substrate added in the first step (20 mg COD l^{-1}). The toxicity level of the tested compound can be assessed by comparing the OUR profiles obtained in runs 1 and 3.

d) Run 4: The fourth step is completed with the addition of a pulse formed by the control substrate (20 mg COD l^{-1}) and the tested compound (with the same concentration as in run 2). Before run 4, biomass used in this run is changed in order to avoid possible interferences due to the previous runs. Runs 1 and 4 are compared for inhibition assessment.

The biodegradation parameters used to compare the four OUR profiles (Figure V.24) obtained in each experiment are the oxygen consumption (OC) and the maximum value of the OUR profile (OUR_{MAX}). The toxic and inhibitory levels can be quantified according to Equations V.9 and V.10

$$\% toxicity = \left(\frac{(OC)_{run1} - (OC)_{run3}}{(OC)_{run1}} \right) \cdot 100 \qquad \text{Equation V.14}$$

$$\% inhibition = \left(\frac{(OUR_{MAX})_{run1} - \left[(OUR_{MAX})_{run4} - (OUR_{MAX})_{run2} \right]}{(OUR_{MAX})_{run1}} \right) \cdot 100 \qquad \text{Equation V.15}$$

V.2.3 Respirometric experiments.

Respirometric tests were used as screening tool to asses the biodegradability, toxic or inhibitory effect of the intermediates coming CWAO over the activated sludge of a municipal WWTP. Two sets of respirometric experiments were performed. In the first set, the respirometer was seeded with a non-acclimatised biomass coming from Tarragona's WWTP. The objective was to obtain the biodegradation parameters of each AC main intermediate coming CWAO with a non-acclimatised population. Later, after 125 days of operation of the pilot plant, a second set of respirometric experiments was performed with the biomass of the pilot scale WWTP to verify the adaptation of this biomass to certain specific intermediates coming from *o*-cresol CWAO.

For each respirometric test, the sludge was aerated overnight to ensure the biomass was under endogenous conditions before each respirometric experiment. 20 mg l^{-1} of 1-allyl-2-thiourea (ATU) was added to avoid any interference due to nitrifying biomass. The determination of total suspended solids (TSS) and volatile suspended solids (VSS) were done according to the standard methods 2540D and 2540E [87]. The average value of biomass concentration in the respirometric experiments was 3400±300 mg VSS l^{-1}.

Respirometric experiments were completed before and after each CWAO experiment to obtain their biodegradation parameters. Moreover, a respirometric experiment was conducted with each intermediate of the CWAO step to determine its biodegradability. In all the respirometric experiments, the added concentration of each CWAO effluent correspond to the measured COD, whereas the added concentration for each pure compound correspond to the ThOD calculated using the empirical correlations obtained by Baker et al. [119].

The biodegradability of the twelve CWAO effluents from phenol, o-cresol and 2-chlorophenol was estimate by respirometry tests using a concentration of 20 mg COD l^{-1}. The biodegradability and the toxic or inhibitory effects of the model compounds (phenol, 2-chlorophenol and *o*-cresol) were tested at 2 and 8 mg COD l^{-1} and the quinone-like intermediates such as catechol, hydroquinone and *p*-benzoquinone were tested at 1 and 4 mg COD l^{-1}.

The biodegradability of the carboxylic acids detected previously was tested at 5 mg COD l^{-1}. These acids were: glyoxylic, oxalic, formic, malonic, acetic, maleic (and its isomer fumaric acid), succinic, propionic and 4-hydroxybenzoic acid (4-HB). After that, the acids were classified in readily and non-readily biodegradable acids. Then, the heterotrophic yield coefficient (Y_H) for the readily biodegradable acids was obtained with respirometric tests at different concentrations (between 2 and 20 mg COD l^{-1}). The other acids were tested again at 5 mg COD l^{-1} to verify their toxic or inhibitory effects.

The concentrations of the compounds used in the respirometric tests were chosen taking into account two items. First, the use of a low load ratio leads to short-term experiments since the substrate is rapidly assimilated and no significant biomass growth occurs [146]. Secondly, the aerobic treatment of the CWAO wastewater will be done in a CSTR, which means that the concentration of the main compounds inside the reactor will be the same than in the effluent and these concentrations must be below the discharge limits if the efficiency in the CSTR is high.

All the respirometric data presented here corresponds to the arithmetic average of the results derived from two equal experiments. The reproducibility of the results and the match (within 10%) between successive experiments was excellent.

V.2.4. Experimental sep-up for the aerobic treatment

To study the feasibility of the coupled CWAO-aerobic treatment of phenolic effluents, a pilot activated-sludge plant was constructed. The design was made by scaling down the

Tarragona WWTP located in the Tarragona, Catalonia (Spain). This facility serves 140000 inhabitants equivalent and its main operational parameters are: a Hydraulic Retention Time (HRT) of 9.6 hours, a Sludge Retention Time (SRT) of 8 days and an average Organic Loading Rate (OLR) of 0.35 g COD g^{-1} VSS d^{-1}. The Volatile Suspended Solid (VSS) concentration in the reactors is 4000 mg VSS l^{-1} whereas its average Sludge Volumetric Index (SVI) is 65 ml g^{-1}. The average influent and effluent COD concentrations obtained in Tarragona's WWTP are 500 and 70 mg l^{-1}, respectively. The pilot activated-sludge plant is schematically drawn in Figure V.25, some pictures can be found in Annex I.

The bioreactor of the pilot plant consists of a Continuous Stirred Tank Reactor (CSTR) with a volume of 40 l, however the experiments were done using 20 l. Air was supplied continuously in order to maintain a S_O in the reactor between 2 and 5 mg l^{-1}. The bioreactor has S_O and pH sensors ((Dulcotest DO 1-mA and Dulcotest PHEX 112 SE, Prominent, Spain)) that are connected to probe indicators-controllers (Dulcometer D1C, Prominent, Spain). pH is left uncontrolled whereas S_O is controlled through manipulation of the pneumatic valve using an ON/OFF control directly programmed into the S_O controller. The PC served as a merely recorder using a virtual instrument programmed in National Instrument LabView 7.0®. The settler with a maximum volume of 60 l was designed maintaining the height to diameter relation of the Tarragona WWTP. The settler area was calculated using an overflow rate (T_s) estimated trough empirical correlations [147]. The pilot plant was located inside a laboratory where the temperature was maintained at 25±1ºC through the air conditioning system.

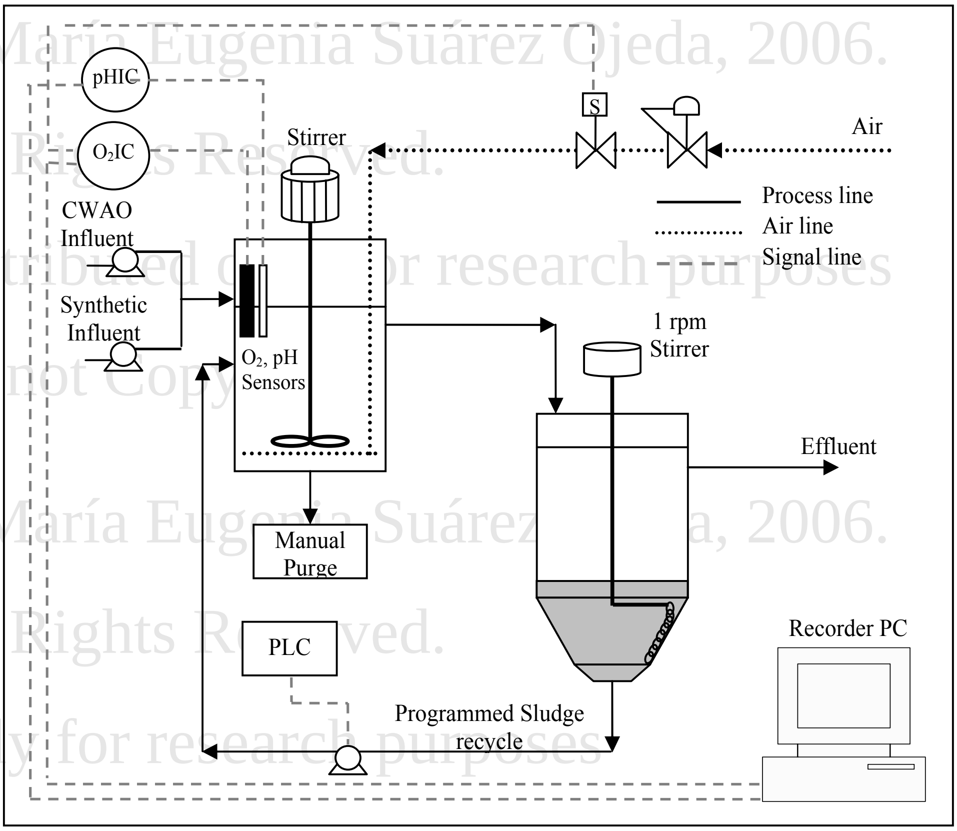

Figure V.25. Pilot Plant Layout

V.2.5 Aerobic treatment inoculation, starting-up and monitoring

The pilot plant was inoculated with sludge from Tarragona’s WWTP and its main operational parameters (HRT, SRT, OLR and VSS concentration) were maintained at similar values than those of Tarragona’s WWTP.

The pilot plant began with an adaptation period to a synthetic wastewater with a composition adapted from Carrera et al. [148], which is similar to the original influent to Tarragona’s WWTP. This period covered the first 10 days of experimentation. Later, as Table V.22 shows, another period has been started in order to follow the plant behaviour in front of increasing loads of CWAO effluents. The parameters used to monitor the pilot plant were the COD effluent concentration, the organic loading rate (OLR), the VSS concentration in the reactor and the SVI.

Moreover, at the end of the CWAO adaptation period, several off-line respirometric tests have been performed to some CWAO intermediates. The objective was to reveal changes in the way that microorganisms metabolise these specific intermediates. The target intermediates were selected as representative of several groups (as will be described later): readily biodegradable intermediates (acetic acid), inert intermediates (maleic acid), toxic or inhibitory intermediates (catechol, hydroquinone and p-benzoquinone) and model compounds (o-cresol and phenol).

For maleic acid the COD_{added} was 5 mg COD l^{-1}, whereas catechol, hydroquinone and p-benzoquinone the COD_{added} was 4 mg COD l^{-1}; in the case of phenol and o-cresol the COD_{added} tested was 8 mg COD l^{-1}. Finally for acetic acid, the heterotrophic yield coefficient was determined using a COD_{added} of 10, 15 and 20 mg COD l^{-1}. The results will be compared to those obtained with the same compounds, concentrations and procedure but using the activated sludge without the adaptation period, i. e. directly coming from the Tarragona WWTP.

V.3. Results and Discussion.

Biodegradability respirometric tests were conducted with each CWAO effluent and with each intermediate compound to determine its individual biodegradability. These preliminary tests (Annex II) allowed classifying the intermediates into two groups: readily biodegradable intermediates and non-readily biodegradable intermediates. The intermediates presenting a similar OC (for the same initial COD concentration) to the acetic acid, which is a classical example of readily biodegradable compound, were considered as readily biodegradable intermediates: fumaric, propionic, acetic, succinic, formic and glyoxylic acids. The procedure explained in section V.2.2 was applied to the rest of intermediates to check their behaviour as inert, toxic or inhibitory compound.

The discussion is divided into four sections. Firstly, the Y_H determination with non-acclimatised sludge for readily biodegradable acids is presented. Next, the biodegradation parameters with non-acclimatised sludge for the rest of acids, the quinone-like products and the phenol and o-cresol are discussed. After that, the behaviour of the pilot scale WWTP treating the o-cresol CWAO effluents as a part of its influent and finally, the respirometric results with acclimatised sludge for a selected CWAO intermediates are presented.

V.3.1 Readily biodegradable acids: heterotrophic yield coefficient determination.

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 framework, the Y_H represents the fraction of substrate used for production of new biomass [149].

The OC could be directly related with the Y_H according to Equation V.11 (considering that all the COD_{added} is consumed):

$$OC = COD_{added} \cdot (1 - Y_H) \quad \text{Equation V.16}$$

Therefore, the Y_H could be easily assessed [150, 151, 68] by conducting several respirometric tests at different concentrations and by finding the linear correlation existing between the OC and the COD_{added}. Table V.18 shows the conditions of the respirometric tests and the Y_H for each readily biodegradable compound. As example, Figure V.26 shows the results obtained for fumaric acid.

Table V.18. Y_H determination results from biodegradability respirometric tests performed at 31ºC and pH = 7.5 ± 0.5. The error of the yield coefficient was calculated from the linear regression.

Acid	COD_{added} (mg COD l^{-1})	R^2	Y_H
Fumaric	2, 5 10, 15	0.996	0.74 ± 0.01
Propionic	5, 10, 15, 20	0.991	0.63 ± 0.02
Acetic	5, 10, 15, 20	0.964	0.71 ± 0.01
Succinic	2, 5, 10, 15	0.943	0.72 ± 0.03
Formic	2, 5, 10, 20	0.940	0.76 ± 0.02
Glyoxylic	2, 5, 10, 15	0.938	0.72 ± 0.02

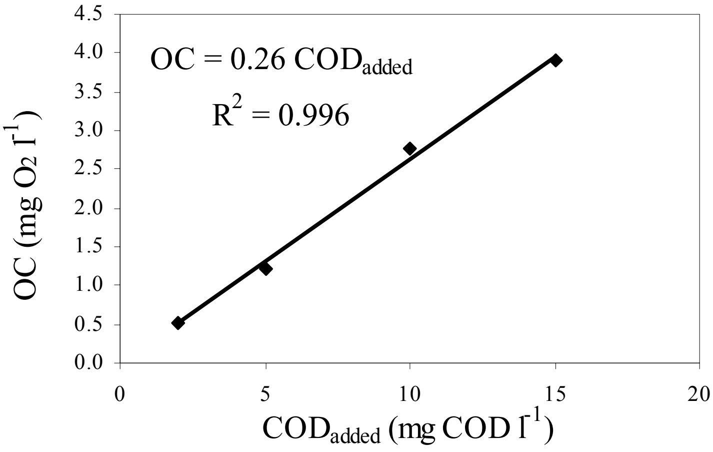

Figure V.26. Y_H determination for fumaric acid: OC vs. added COD.

Finally, an average Y_H was calculated with all the values of Table V.18 ($\overline{Y_H}$ = 0.71 mg COD mg^{-1} COD). The $\overline{Y_H}$ was used to estimate the readily biodegradable COD (COD_{RB}) of each CWAO effluent as will be explained in section V.3.3 in this chapter. The $\overline{Y_H}$ obtained in this study was in the range of the values reported in the literature (0.64-0.79 mg COD mg^{-1} COD) [150, 152]. However, the Y_H depends on the substrate as well as on the population of microorganisms, so direct comparison of literature values to those obtained in this work is not straightforward and must be done with care.

V.3.2 Inert intermediates and toxic or inhibitory intermediates behaviour.

There were some CWAO intermediates that seem to be non-readily biodegradable but they did not have any toxic or inhibitory effect. These intermediates were classified as inert intermediates. Additionally, other CWAO intermediates had a negative effect on the OC and the OUR_{MAX} of the control substrate, indicating a toxic or inhibitory behaviour.

The biodegradation parameter determination by means of a respirometric experiment, as described in section V.2.2 this chapter, was performed for all the non-readily biodegradable intermediates: carboxylic acids (oxalic, maleic, malonic, 4-HB and salicylic acids), quinone-like compounds (catechol, hydroquinone and *p*-benzoquinone) and model compounds (phenol, 2-chlorophenol and *o*-cresol). Figure V.27 to Figure V.29 show the OUR profiles obtained for each compound whereas the numerical results are presented in Table V.19 to Table V.21.

The respirometric experiments with 5 mg COD l^{-1} of oxalic, maleic, malonic, 4-HB and salicylic acids (tests 2, Table V.19) demonstrated that these compounds were non-readily biodegradable because there was no OC. Moreover, in the most of these acids, the biodegradation parameters (OUR_{MAX} and OC) of tests 1, 3 and 4 were similar (less than the 10% fixed as acceptable reproducibility) and no toxic or inhibitory effect could be observed. Hence, these carboxylic acids were classified as inert intermediates. In agreement with this result, Stowell et al. [153] found that oxalic acid was a non-biodegradable intermediate of the ozonation of 2-chlorophenol. However, it would be possible that these acids were actually slowly biodegradable or cometabolically degraded. For instance, the 4-HB acid showed a high increase in the biodegradation parameters in test 4 compared to test 1. This increase in the OC and OUR_{MAX} could be due to a cometabolic biodegradation of 4-HB acid with acetate. It is known that non-readily biodegradable substrates, such as 4-HB acid, can be biodegraded through cometabolic pathways [154, 155]. Long-term experiments, instead of respirometric tests (short-term experiments), are necessary to confirm this possibility.

Regarding to quinone-like intermediates, the OC in test 2 with 1 and 4 mg COD l^{-1} of catechol (Table V.20) demonstrated that this compound was, surprisingly, more biodegradable than oxalic, maleic, malonic and 4-HB acids. Moreover, Table V.20 shows that the OC was, approximately, 20% higher in test 3 than in test 1, indicating that there was no toxicity due to catechol. This increase in the OC could be due to a cometabolic biodegradation of catechol with acetate. However, the decrease in the OUR_{MAX} in test 1 (0.8 mg O_2 l^{-1} min^{-1}) comparing to test 4 (0.5 mg O_2 l^{-1} min^{-1}) in the respirometric test with 4 mg COD l^{-1} of catechol was a sign of inhibition. On the other hand, the OC in tests 2 with 1 and 4 mg COD l^{-1} of hydroquinone and *p*-benzoquinone (Table V.20) demonstrated that these compounds were non-readily biodegradable intermediates. In addition, the high decrease in the OC and OUR_{MAX} in the respirometric experiments with 4 mg COD l^{-1} of both compounds (Table V.20) indicated that hydroquinone and *p*-benzoquinone had a high toxic effect at this concentration. Nevertheless, the toxic effect was not detected at 1 mg COD l^{-1} of both compounds (Table V.20).

Consequently, catechol, hydroquinone and *p*-benzoquinone had behaviour of inert intermediates at 1 mg COD l^{-1} but they became inhibitory (catechol) or toxic (hydroquinone and *p*-benzoquinone) intermediates at 4 mg COD l^{-1}. According to this result, Santos et al. [132] found that hydroquinone and *p*-benzoquinone were the most toxic intermediates in the CWAO of phenol using a commercial copper-based catalyst. However, the toxicity determined by Santos et al. [132] with the Microtox® test was higher than the toxic effect determined by respirometry in this work. For instance, they found an EC_{50} of 0.041 mg l^{-1} for hydroquinone after 15 min contact time. The EC_{50} is defined as the effective nominal concentration of toxicant that reduces the intensity of light emission of *Vibrio fischeri* by 50%. However, the respirometry with 1 mg COD l^{-1} of hydroquinone (0.53 mg l^{-1} of compound) did not show any toxic effect on the biomass after more than 100 min of contact time. This result shows that Microtox® determinations could give an overestimation of the toxicity comparing to respirometric tests done with biomass from a municipal WWTP.

Finally, the respirometric experiments for model compounds (tests 2, Table V.19) demonstrated that these compounds were non-readily biodegradable because there was not OC. Besides, Table V.19 shows that all the OC in tests 3 was higher than the OC in tests 1, indicating that there was no toxicity at the tested concentrations and, probably, phenol, 2-chlorophenol and *o*-cresol were cometabolically degraded with acetate. Additionally, an inhibitory effect was detected in the experiment with 8 mg COD l^{-1} for *o*-cresol because the OC and OUR_{MAX} (Table V.19) were 30 and 50% lower in test 4 than in test 1, respectively.

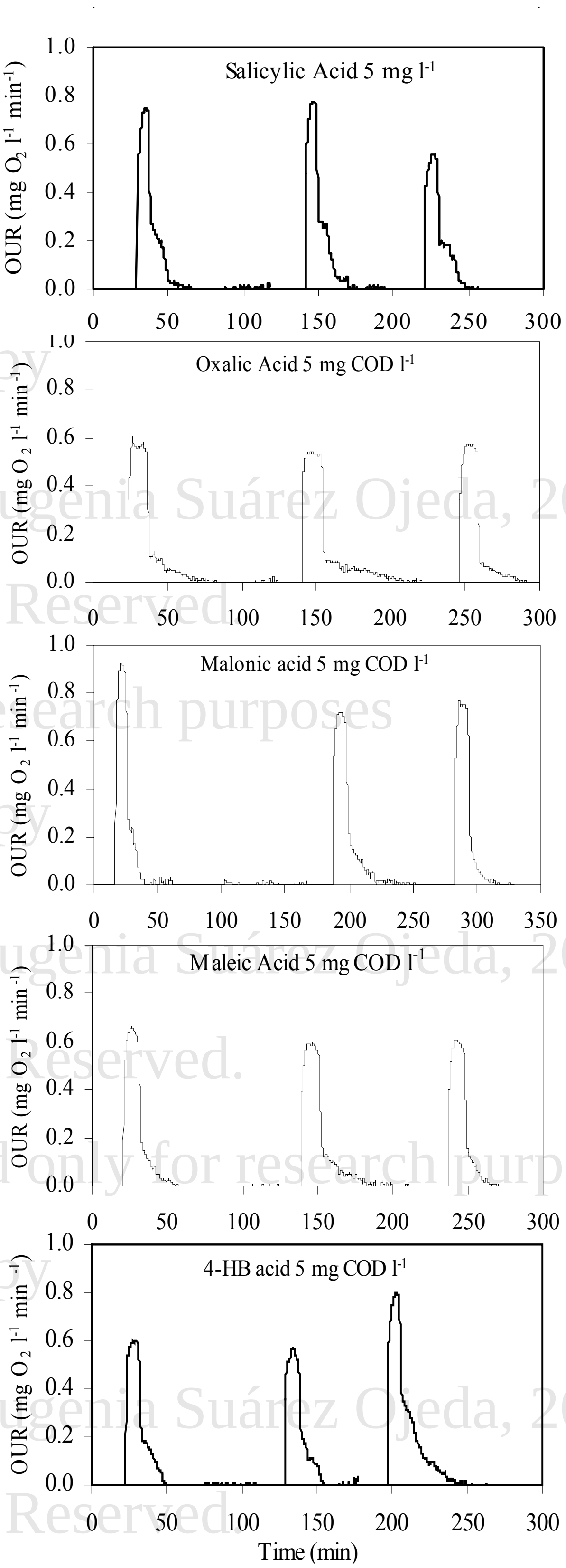

Figure V.27. OUR profiles for oxalic acid, malonic acid, maleic acid, 4-HB and salicylic acid. All profiles were obtained with 5 mg COD l^{-1}.

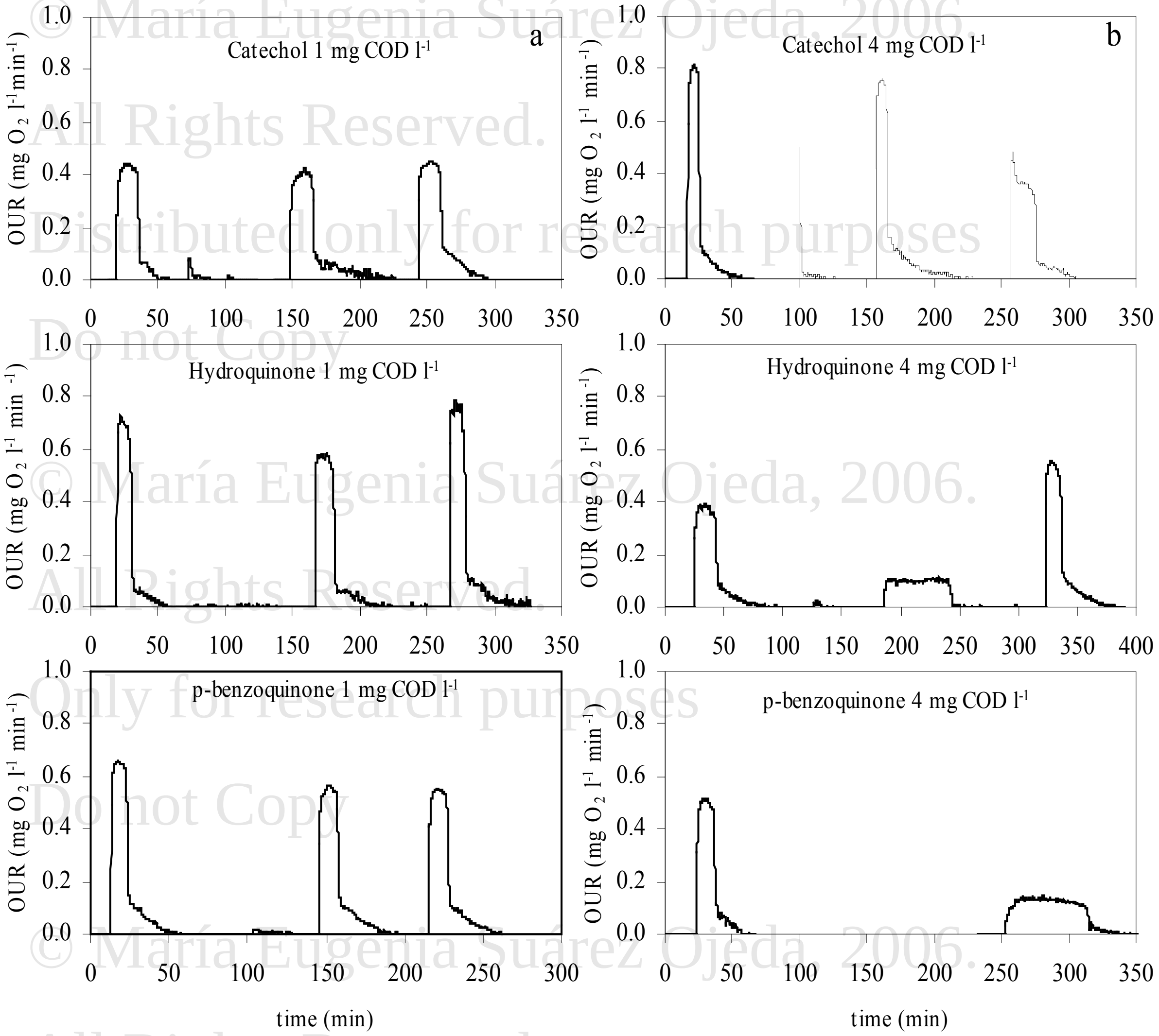

Figure V.28. OUR profiles for catechol, hydroquinone and *p*-benzoquinone. Figures on the left column (Figure V.28a) were obtained with 1 mg COD l^{-1} and figures on the right column (Figure V.28b) were obtained with 4 mg COD l^{-1}.

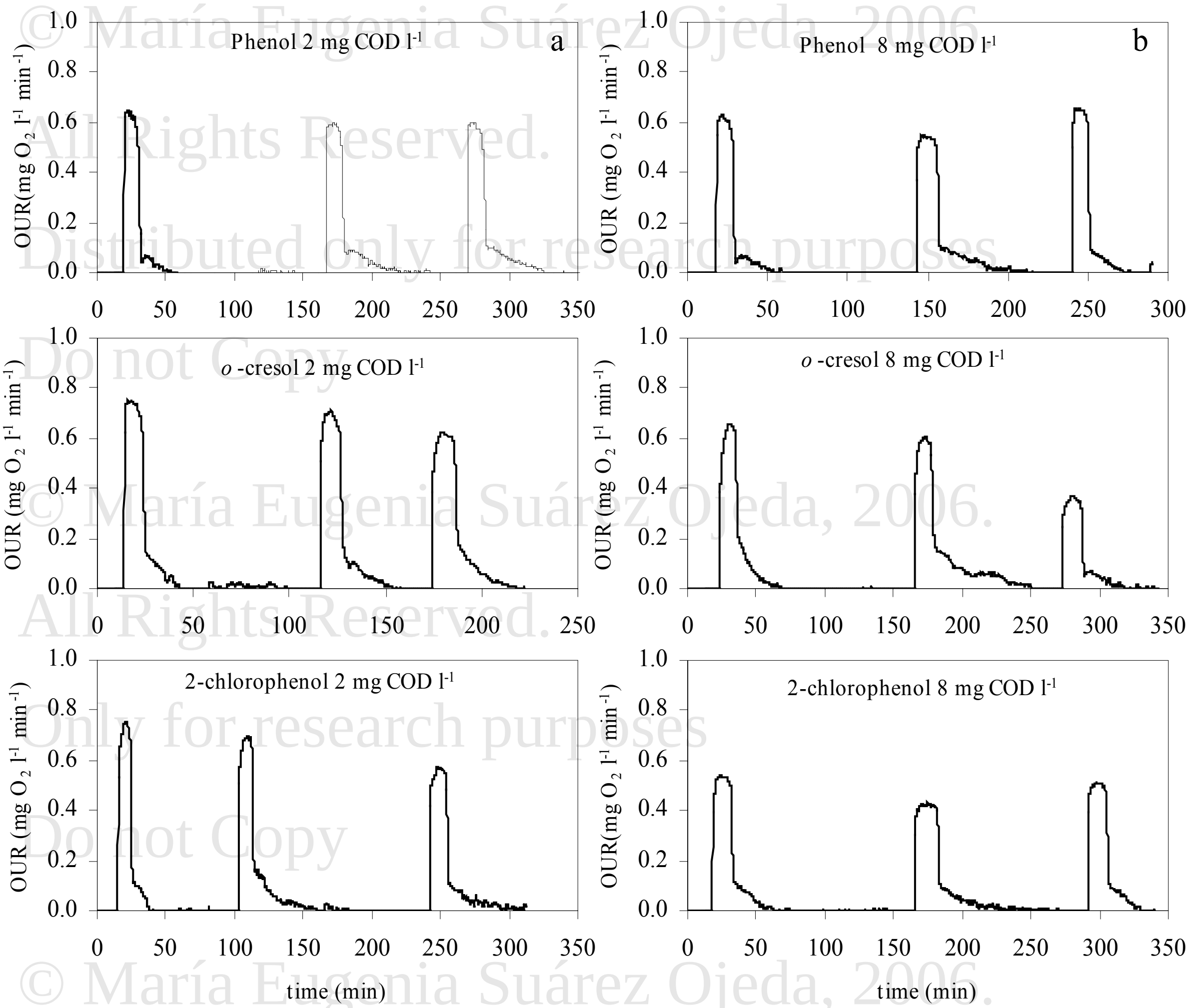

Figure V.29. OUR profiles for phenol, *o*-cresol and 2-chlorophenol. Figures on the left column (Figure V.29a) were obtained with 1 mg COD l^{-1} and figures on the right column (Figure V.29b) were obtained with 4 mg COD l^{-1}.

Table V.19. Biodegradation parameters obtained for some carboxylic acids: salicylic, oxalic, maleic, malonic and 4-HB acids.

Run number	1	2	3	4
Substrate pulse	acetate	salicylic acid	acetate	acetate + salicylic acid
COD_{added} (mg COD l^{-1})	20	5	20	20 + 5
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.8	0.6
OC (mg O_2 l^{-1})	7.9	0.0	8.5	7.2
Substrate pulse	acetate	oxalic acid	acetate	acetate + oxalic acid
COD_{added} (mg COD l^{-1})	20	5	20	20 + 5
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.6	0.0	0.5	0.6
OC (mg O_2 l^{-1})	9.0	0.0	9.7	8.0
Substrate pulse	acetate	maleic acid	acetate	acetate + maleic acid
COD_{added} (mg COD l^{-1})	20	5	20	20 + 5
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.5
OC (mg O_2 l^{-1})	8.3	0.0	9.1	7.6
Substrate pulse	acetate	malonic acid	acetate	acetate + malonic acid
COD_{added} (mg COD l^{-1})	20	5	20	20 + 5
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.9	0.0	0.7	0.8
OC (mg O_2 l^{-1})	9.8	0.0	9.7	9.5
Substrate pulse	acetate	4-HB acid	acetate	acetate + 4-HB acid
COD_{added} (mg COD l^{-1})	20	5	20	20 + 5
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.6	0.0	0.6	0.8
OC (mg O_2 l^{-1})	7.1	0.0	7.1	11.1

Table V.20. Biodegradation parameters obtained for quinone-like intermediates: catechol, hydroquinone and *p*-benzoquinone.

Test number	1	2	3	4
Substrate pulse	acetate	catechol	acetate	acetate + catechol
COD_{added} (mg COD l^{-1})	20	1	20	20 + 1
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.4	0.1	0.4	0.5
OC (mg O_2 l^{-1})	7.3	0.3	8.7	9.1
COD_{added} (mg COD l^{-1})	20	4	20	20 + 4
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.8	0.5	0.8	0.5
OC (mg O_2 l^{-1})	7.8	0.6	9.2	7.7
Substrate pulse	acetate	hydroquinone	acetate	acetate + hydroquinone
COD_{added} (mg COD l^{-1})	20	1	20	20 + 1
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.8
OC (mg O_2 l^{-1})	8.2	0.0	8.9	10.2
COD_{added} (mg COD l^{-1})	20	4	20	20 + 4
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.4	0.0	0.1	0.6
OC (mg O_2 l^{-1})	8.2	0.0	5.7	9.0
Substrate pulse	acetate	*p*-benzoquinone	acetate	acetate + *p*-benzoquinone
COD_{added} (mg COD l^{-1})	20	1	20	20 + 1
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.6
OC (mg O_2 l^{-1})	8.1	0.2	8.4	8.0
COD_{added} (mg COD l^{-1})	20	4	20	20 + 4
OUR_{MAX} (mg O_2 l^{-1} min–1)	0.5	0.0	0.0	0.1
OC (mg O_2 l^{-1})	7.4	0.0	0.0	7.8

Table V.21. Biodegradation parameters obtained for phenol, 2-chlorophenol and *o*-cresol.

Test number	1	2	3	4
Substrate pulse	acetate	phenol	acetate	acetate + phenol
COD_{added} (mg COD l^{-1})	20	2	20	20 + 2
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.6
OC (mgO_2 l^{-1})	7.2	0.0	8.8	9.5
COD_{added} (mg COD l^{-1})	20	8	20	20 + 8
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.6	0.0	0.5	0.7
OC (mg O_2 l^{-1})	7.3	0.0	9.3	7.5
Substrate pulse	acetate	2-chlorophenol	acetate	acetate+2-chlorophenol
COD_{added} (mg COD l^{-1})	20	2	20	20 + 2
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.8	0.0	0.7	0.6
OC (mg O_2 l^{-1})	7.5	0.0	9.1	8.7
COD_{added} (mg COD l^{-1})	20	8	20	20 + 8
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.5	0.0	0.4	0.5
OC (mg O_2 l^{-1})	9.0	0.0	9.2	8.5
Substrate pulse	acetate	*o*-cresol	acetate	acetate + *o*-cresol
COD_{added} (mg COD l^{-1})	20	2	20	20 + 2
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.8	0.0	0.7	0.6
OC (mg O_2 l^{-1})	8.4	0.0	8.8	9.3
COD_{added} (mg COD l^{-1})	20	8	20	20 + 8
OUR_{MAX} (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.4
OC (mg O_2 l^{-1})	9.5	0.0	11.9	6.3

V.3.3 CWAO effluents biodegradability

As explained in section V.2.3, the biodegradability of the twelve CWAO effluents was estimated by respirometry using a concentration of 20 mg COD l^{-1} (COD_{added}). The dependence of the intermediates distribution and AC behaviour on the operational conditions in the CWAO was discussed in Chapter IV. At this point, this distribution will be correlated with the measured biodegradability of each CWAO effluent in order to find the best condition in the CWAO, which permits a successful coupling with a municipal WWTP.

In any wastewater, the total biodegradable COD (COD_{TB}) is the sum of the readily (COD_{RB}) and the slowly biodegradable COD (COD_{SB}) fractions, in accordance to the original bi-substrate model proposed in the 80s by Dold et al. [156]. The determination of COD_{TB} requires a combination of several techniques and experiments [149, 157] but, specifically the COD_{SB} determination is extremely time-consuming, whereas the available methods for COD_{RB} determination mostly relays in fast respirometric experiments [158]. Therefore, the COD_{RB} can be used as a fast method to characterize the biodegradability of a specific wastewater. In particular, in this study respirometry is used as a screening test to compare the biodegradability enhancement reached with different oxidation conditions with respect to the initial model compounds effluents.

The readily biodegradable COD (COD_{RB}) of each CWAO effluent can be estimated using the $\overline{Y_H}$ calculated in section V.3.1 this chapter, by using the following equation [150, 151, 158]:

$$COD_{RB} = \frac{OC_m}{1 - Y_H}$$ Equation V.17

being OC_m the measured value obtained from respirometry.

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

$$\%COD_{RB} = \frac{COD_{RB}}{COD_{added}} \cdot 100$$ Equation V.18

Figure V.30 shows the $\%COD_{RB}$ and intermediates distribution of each one of the twelve CWAO effluents for phenol, *o*-cresol and 2-chlorophenol. This figure showing the intermediates distribution is similar to the presented in chapter IV, but the intermediates distribution is adapted to the terms defined in sections V.3.1 and V.3.2 this chapter.

As usual, during the discussion the CWAO conditions will use the following nomenclature: 140-2 will refers to 140ºC and 2 bar of oxygen partial pressure, 160-9 equals to 160ºC and 9 bar of oxygen partial pressure and so on.

Three different features should be considered when selecting the most suitable CWAO condition: the maximum COD conversion obtained in the CWAO, the maximum $\%COD_{RB}$ and the catalyst preservation. For phenol effluents, at 140-2 and 140-9, there was low biological consumption, probably because the high remaining phenol concentration could be inhibiting it. The maximum $\%COD_{RB}$ (36%) occurred at a CWAO condition of 160-2. From Figure V.30a, at this condition, the readily biodegradable acids have a maximum concentration, whereas the possible toxic/inhibitory intermediates (catechol, hydroquinone and *p*-benzoquinone) have a low concentration. At 160-9, the $\%COD_{RB}$ (15%) was lower than the previous case; the readily biodegradable intermediates were in lower proportion whereas the possible toxic/inhibitory intermediates were in higher proportion. For phenol, the maximum COD conversion (chapter IV) and the maximum COD_{RB} were obtained at 160-2. Additionally, the AC conservation is clearly higher at 2 bar than at 9 bar (chapter IV). Based on these results, 160-2 should be the most suitable CWAO condition for phenol oxidation.

For *o*-cresol effluents, there was no biodegrability at 140-2 because the remaining *o*-cresol concentration was the highest and the readily biodegradable concentration was almost negligible (Figure V.30b). For the rest of conditions, the $\%COD_{RB}$ was very similar, being 160-9 the condition which had the highest proportion of readily biodegradable acids and consequently the highest biodegradability, as reflected by the maximum $\%COD_{RB}$ (27%). At 140-9 and 160-2, the biodegradability was similar because the proportion of readily biodegradable, inert and possible toxic/inhibitory intermediates was almost the same.

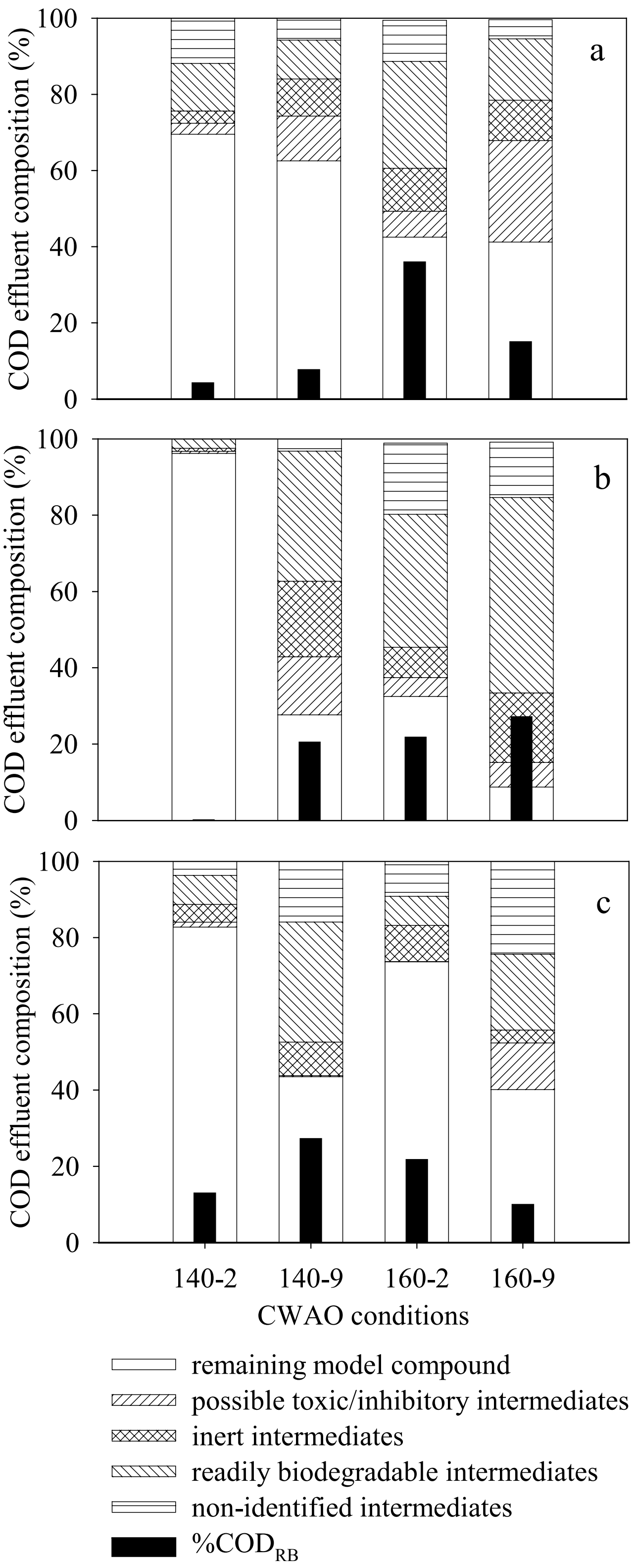

Figure V.30. Intermediates distribution and readily biodegradable COD fraction of phenol (a), *o*-cresol (b) and 2-chlorophenol (c) CWAO effluents.

Hence, the biodegrability for *o*-cresol was similar for whatever condition used in the CWAO (with the exception of 140-2). The final selection of the most suitable CWAO condition could be subjected either to the maximum COD conversion or to the catalyst preservation. In this case, the maximum COD conversion was obtained at 160-9 but there was not a significant difference with 160-2 (chapter IV). Nevertheless, the AC conservation was clearly higher at 160-2 than 160-9 (chapter IV). As a result, 160-2 could be the most adequate CWAO condition for *o*-cresol oxidation.

Finally for 2-chlorophenol, the lowest $\%COD_{RB}$ (10%) occurred at 160-9 (Figure V.30c), despite the significant concentration of readily biodegradable acids. In fact, this case was the only one with hydroquinone and *p*-benzoquinone as intermediates. Therefore, the toxic effect of these quinones could be a possible cause in the decrease of biodegradability. In addition, the proportion of non-identified compounds, which was around 24%, should be considered. From HPLC chromatograms, the most of them were in the retention times of quinone-like and aromatic compounds, so that they are expected to be toxic or inhibitory intermediates. The highest $\%COD_{RB}$ (27%) was obtained at 140-9 because there was the highest proportion of readily biodegradable acids and the lowest proportion of remaining 2-chlorophenol. However, the $\%COD_{RB}$ (22%) at 160-2 was very similar to the obtained at 140-9. From this results, it can be concluded that the only important biodegradability enhancement for 2-chlorophenol occurred at 140-9 and at 160-2. Consequently, the final selection of the most suitable CWAO condition is subjected again to the maximum COD conversion and the catalyst preservation. Once more, 160-2 could be the most adequate CWAO condition for 2-chlorophenol oxidation because had a higher COD conversion and an acceptable AC conservation (chapter IV).

Overall, it could be concluded that the best CWAO condition for phenol, *o*-cresol and 2-chlorophenol is 160ºC and 2 bar of P_{O2}. At this condition, the COD conversion was the highest one for phenol and 2-chlorophenol and the second one for *o*-cresol (chapter IV). The catalyst preservation was clearly better than the oxidation at 9 bar of P_{O2} (chapter IV). Finally, the $\%COD_{RB}$ was the highest for phenol and almost the maximum for *o*-cresol and 2-chlorophenol. Moreover, the $\%COD_{RB}$ of the effluents from 160-2 (22-36%) were slightly higher than those obtained in the characterisation of other industrial wastewaters treated biologically in WWTPs. For instance, Arslan and Ayberk [159] found a $\%COD_{RB}$ between 3-24% for a wastewater that included raw domestic wastewater and pre-treated industrial wastewaters of various sectors such as tyre, drug or chemistry. Ubay Çokgór et al. [151] presented the $\%COD_{RB}$ for several untreated industrial wastewaters: textile (15%), tannery

(16%) and meat processing (13%). This comparison shows that the effluents obtained at 160-2 can be treated in a municipal WWTP. Taking into account that the COD_{RB} is only a part of the COD_{TB} of a particular wastewater, this comparison shows that the effluents obtained at 160-2 could be efficiently managed and treated in a municipal WWTP if they only mean a properly selected part of the total influent to the WWTP.

On the other hand, the results presented in this work show that the biodegradability of a CWAO effluent could be predicted knowing its composition and the concentration of the main intermediates. In general, if the concentration of some carboxylic acids (fumaric, propionic, acetic, succinic, formic and glyoxylic acids) is high, the biodegradability will be high. However, the biodegradability could be strongly affected by the presence of some quinone-like intermediates as hydroquinone or *p*-benzoquinone because of its toxic effect.

V.3.4 Aerobic biological treatment of effluents from AC/CWAO of o-cresol and phenol wastewater.

V.3.4.1 COD Removal and Sludge Settleability Evolution.

The pilot plant study is divided in three periods depending on the percentage of the total influent COD coming from the o-cresol CWAO effluent (5, 15 or 30%). The initial biomass concentration was about 4000 mg VSS l^{-1}whereas the SVI was 65 ml g^{-1}. Figure V.31 shows the plant evolution, whereas Table V.22 shows the average values of the operational parameters monitored in this study. Table V.23 presents the CWAO intermediates detected in the pilot plant effluents during the study. Total influent and effluent COD concentrations and SVI (that indicates the sludge settleability behaviour), which reveals the sludge settleability behaviour, were monitored during more than 100 days, also, the TSS and VSS had been checked during the study; however, the values were always around 4400±300 mg SSV l^{-1}, being the VSS/TSS ratio around 80±10%.

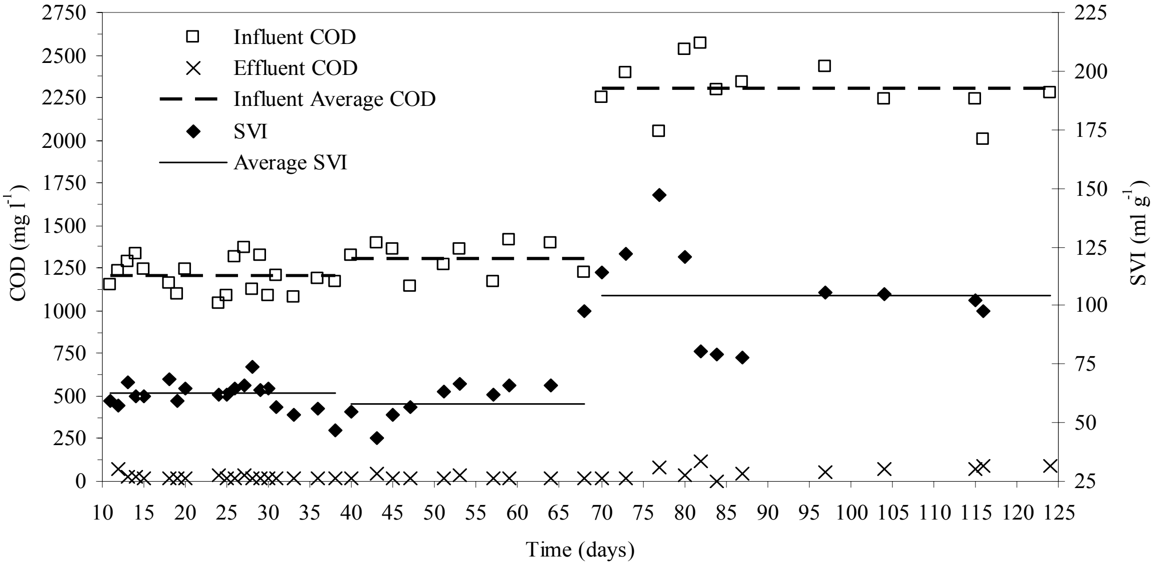

Figure V.31. Evolution of pilot scale municipal WWTP parameters during the 125 days of continuous operation with o-cresol CWAO effluent as a part of the total influent.

Table V.22. Average values of the operational parameters used in this work.

Phase	Days	[VSS] (mg l^{-1})	[Influent] (mg COD l^{-1})	% of Influent from CWAO	[Effluent] (mg COD l^{-1})	OLRT (mg COD mg VSS^{-1} d^{-1})	SVI (ml $^{l-1}$)
1	31	4298±200	1156±20	5	26±10	0.32±0.02	63±5
2	28	4134±300	1318±20	15	24±10	0.38±0.03	58±8
3	54	4698±200	2318±30	30	64±30	0.59±0.03	104±20

Table V.23. CWAO intermediates detected at the plant effluent during successive operating periods.

Intermediate	Period 1 (mg l^{-1})	Period 1 (mg COD l^{-1})	Period 2 (mg l^{-1})	Period 2 (mg COD l^{-1})	Period 3 (mg l^{-1})	Period 3 (mg COD l^{-1})
Malonic acid	34.9	21.5	7.6	4.7	8.5	5.3
Maleic acid	0.3	0.2	0.5	0.7	0.3	0.2
Salicylic (2-HB) acid	0.0	0.0	0.3	0.5	0.3	0.5
2',2'-Biphenol	0.0	0.0	0.2	0.4	0.4	0.9
Phenol	0.0	0.0	6.1	13.5	16.2	32.1
o-Cresol	0.0	0.0	3.5	8.8	7.3	18.3

As can be seen in Figure V.31, the effluents COD concentration never surpassed the COD discharge limit fixed by the EU (125 mg COD l^{-1} [20]), although the pilot scale WWTP worked in the range of the typical OLR for municipal WWTP [160]. For instance, the total effluent COD of period 3 was 64±30 mg COD l^{-1} and the HPLC analysis of this effluent showed that this low COD was, basically, in form of: phenol (32 mg COD l^{-1}), o-cresol (18 mg COD l^{-1}) and malonic acid (6 mg COD l^{-1}). The rest of intermediates were completely biodegraded, which means that some of the carboxylic acids classified as inert intermediates by respirometry are slowly biodegradable compounds. Also, the results indicate that the malonic acid was not biodegraded while the removal of COD in form of o-cresol and phenol was 92 and 64%, respectively. The removal efficiency of both phenolic compounds was quite high but it can be remarked that it was probably due to the low percentage of the whole COD coming from o-cresol and phenol and their co-metabolic biodegradation with readily biodegradable compounds. The increase in the removal of phenolic compounds between period 2 and 3 could be due to the progressive acclimatisation of the pilot plant sludge to phenolic compounds.

From Figure V.31, in the period 1 and period 2, the settleability of the sludge (SVI) was not affected by the addition of 5 (period 1) or 15% (period 2) CWAO effluents in the inlet to the plant. In fact, from Table V.22, there were no significant changes in the average SVI in both periods (63 ml g^{-1} in period 1 and 58 ml g^{-1} for period 2) compared to the original one (65 ml g^{-1}). At the third and last period with 30% CWAO effluents in the inlet to the plant, the SVI (Figure V.31) increases dramatically till a value around 145 ml g^{-1} in day 67 after 1 week of operation at this proportion of CWAO effluents (30%). This increase could be due to some toxic effect over the biomass, therefore the sludge purge was slowed down by a half until the system recovered and returned to normal operation being the average SVI (Table V.22) of 104 mg l^{-1}. In any case the system never exceeded the SVI value of 150 mg l^{-1}, beyond that value, the sludge settleability is considered very poor [160].

In context of integrated management of high- strength o-cresol wastewater, in the case of period 3 the results mean more than 99% in COD removal from the initial o-cresol : from 9500 mg l^{-1} to just only 64 mg l^{-1}. In terms of o-cresol removal, the integrated process is capable of pass from 5000 mg l^{-1} to only 7 mg l^{-1} that is 99.9% o-cresol removal (Figure V.32). However is should be pointed out that the discharge limit for industrial wastewater in a municipal collector is 1500 mg COD l^{-1} [20], therefore, if the initial COD is kept, the CWAO reacting conditions should be changed, by adding, for example, a recirculation loop.

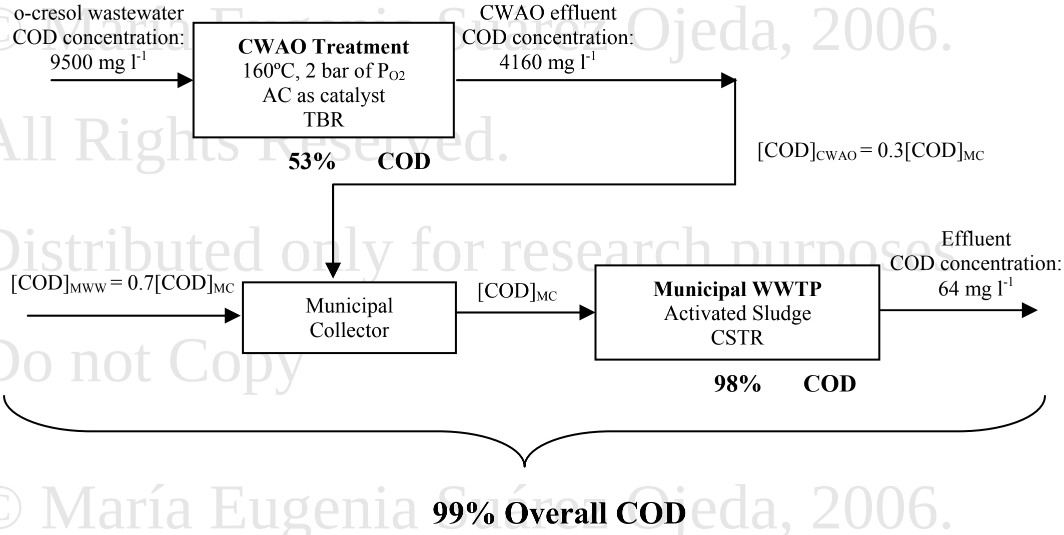

Figure V.32. Schematic view of an integrated treatment of high strength o-cresol wastewater

V.3.4.2 Off-line respirometry results with acclimatised sludge coming from the pilot plant

The determination of biodegradation parameters by means of a respirometric experiments using activated sludge from the pilot plant, as described in section V.2.2, was performed for a selected group of CWAO intermediates, namely maleic and acetic acids, quinone-like compounds (catechol, hydroquinone and *p*-benzoquinone) and model compounds (phenol and *o*-cresol). The objective was to reveal changes in the way that microorganisms metabolise these specific intermediates after after 125 days treating CWAO effluents.

Table V.24 shows the numerical biodegradation parameters whereas Figure V.33 shows the OUR profiles obtained for each compound with sludge from Tarragona municipal WWTP and from the pilot plant.

Table V.24. Biodegradation parameters obtained for some CWAO intermediates with activated sludge from Tarragona municipal WWTP and from Pilot Plant.

Tarragona municipal WWTP				
Test number	1	2	3	4
Substrate pulse	acetate	maleic acid	acetate	acetate + maleic acid
CODadded (mg COD l^{-1})	20	5	20	20 + 5
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.5
OC (mg O_2 l^{-1})	8.3	0.0	9.1	7.6
Substrate pulse	acetate	catechol	acetate	acetate + catechol
CODadded (mg COD l^{-1})	20	4	20	20 + 4
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.8	0.5	0.8	0.5
OC (mg O_2 l^{-1})	7.8	0.6	9.2	7.7
Substrate pulse	acetate	hydroquinone	acetate	acetate + hydroquinone
CODadded (mg COD l^{-1})	20	4	20	20 + 4
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.4	0.0	0.1	0.6
OC (mg O_2 l^{-1})	8.2	0.0	5.7	9.0
Substrate pulse	acetate	p-benzoquinone	acetate	acetate + p-benzoquinone
CODadded (mg COD l^{-1})	20	4	20	20 + 4
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.5	0.0	0.0	0.1
OC (mg O_2 l^{-1})	7.4	0.0	0.0	7.8
Substrate pulse	acetate	phenol	acetate	acetate + phenol
CODadded (mg COD l^{-1})	20	8	20	20 + 8
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.6	0.0	0.5	0.7
OC (mg O_2 l^{-1})	7.3	0.0	9.3	7.5
Substrate pulse	acetate	o-cresol	acetate	acetate + o-cresol
CODadded (mg COD l^{-1})	20	8	20	20 + 8
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.7	0.0	0.6	0.4
OC (mg O_2 l^{-1})	9.5	0.0	11.9	6.3
Pilot Plant				
Test number	1	2	3	4
Substrate pulse	acetate	maleic acid	acetate	acetate + maleic acid
CODadded (mg COD l^{-1})	20	5	20	20 + 5
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	1.0	0.0	1.1	1.0
OC (mg O_2 l^{-1})	7.2	0.0	7.7	7.1
Substrate pulse	acetate	catechol	acetate	acetate + catechol
CODadded (mg COD l^{-1})	20	4	20	20 + 4
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.6	0.7	0.6	0.7
OC (mg O_2 l^{-1})	6.4	0.7	6.6	7.3
Substrate pulse	acetate	hydroquinone	acetate	acetate + hydroquinone
CODadded (mg COD l^{-1})	20	4	20	20 + 4
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.8	0.2	0.9	0.9
OC (mg O_2 l^{-1})	6.2	1.4	6.8	8.3
Substrate pulse	acetate	p-benzoquinone	acetate	acetate + p-benzoquinone
CODadded (mg COD l^{-1})	20	4	20	20 + 4
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	0.7	0.1	0.7	0.6
OC (mg O_2 l^{-1})	6.8	0.8	7.4	7.5
Substrate pulse	acetate	phenol	acetate	acetate + phenol
CODadded (mg COD l^{-1})	20	8	20	20 + 8
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	1.0	0.4	1.0	1.4
OC (mg O_2 l^{-1})	7.6	3.6	7.4	11.7
Substrate pulse	acetate	o-cresol	acetate	acetate + o-cresol
CODadded (mg COD l^{-1})	20	8	20	20 + 8
OUR$_{MAX}$ (mg O_2 l^{-1} min^{-1})	1.0	0.3	1.1	1.1
OC (mg O_2 l^{-1})	6.9	2.6	7.4	9.2

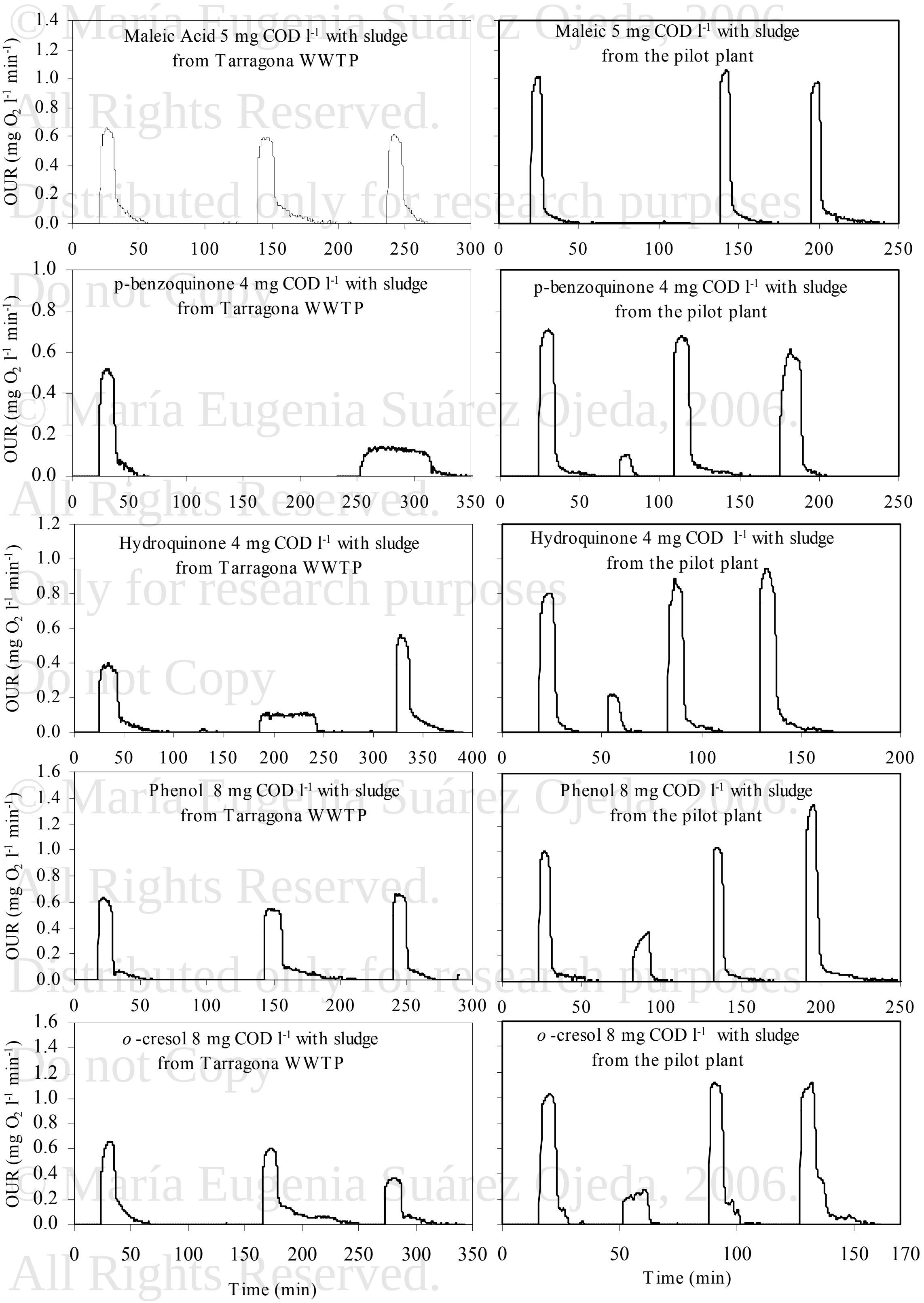

Figure V.33. OUR profiles obtained from the respirometry tests with sludge from Tarragona WWTP (left) and with sludge from the pilot plant (right).

The respirometric experiments of maleic acid with 5 mg COD l^{-1} and pilot plant sludge (tests 2, Table V.24) demonstrated that it was still non-readily biodegradable because there was no OC, in spite of being provided more than 100 days as part of CWAO effluents. This fact is also confirmed by Table V.23, where it can be observed that maleic acid is always present in the pilot plant effluents. However, the biodegradation parameters (OUR_{MAX} and OC) of tests 1, 3 and 4 (Table V.24) with pilot plant sludge were similar (less than the 10% fixed as acceptable reproducibility) and no toxic or inhibitory effect could be observed. The same behaviour was previously obtained with non-acclimatised sludge.

In the case of acetic acid, which was found as a readily biodegradable intermediate, the Y_H obtained for acetic with sludge from Tarragona municipal WWTP was 0.71 ± 0.01 (section V.3.1) and with pilot plant sludge was 0.69 ± 0.01.

For hydroquinone and p-benzoquinone the OC obtained in tests 2 (Table V.24) with pilot plant sludge are above zero, which demonstrated that were partially biodegraded after the adaptation period. With biomass from Tarragona municipal WWTP, the OC previously obtained was zero, indicating no biodegradability of these compounds. Moreover, with pilot plant sludge, Table V.24 shows that the OC was, approximately, 13% higher in test 3 than in test 1, indicating that now there was no toxicity due to hydroquinone or p-benzoquinone. Also, with pilot plant sludge, the OC of tests 4 were between 11 and 34% higher than those obtained in tests 1, which could indicate a cometabolic biodegradation of both compounds with acetate. On the other hand, in the tests 1 compared to tests 3 with 4 mg COD l^{-1} of hydroquinone and *p*-benzoquinone and sludge from Tarragona municipal WWTP, the high decrease in the OC and OUR_{MAX} demonstrated that these compounds had a high toxic effect at this concentration.

In the case of catechol, with sludge from Tarragona municipal WWTP, the OC measured, indicated that catechol was a moderate readily biodegradable compound, but, the decrease in the OUR_{MAX} in test 1 (0.8 mg O_2 l^{-1} min^{-1}) comparing to test 4 (0.5 mg O_2 l^{-1} min^{-1}) was a sign of inhibition. However, making the same comparisons but, with pilot plant sludge, there was no observed any sing of toxicity nor inhibitory effect.

Consequently, with sludge from Tarragona municipal WWTP, catechol, hydroquinone and *p*-benzoquinone became inhibitory (catechol) or toxic (hydroquinone and *p*-benzoquinone) intermediates at 4 mg COD l^{-1}. But, after the adaptation period, the biomass was capable of oxidise these compounds without any sign of toxicity or inhibitory effect.

Finally, the respirometric experiments for o-cresol and phenol (tests 2, Table V.24) with sludge from Tarragona municipal WWTP demonstrated that these compounds were non-readily biodegradable because there was not OC, however, after the adaptation period, the OC were 3.6 and 2.6 mg l^{-1} min^{-1} for phenol and o-cresol, respectively, indicating that the adapted biomass was capable of degrading these compounds at some extent. Besides, with pilot plant biomass, Table V.24 shows that all the OC in tests 3 was higher or equal than the OC in tests 1, indicating that there was no toxicity at the tested concentrations and, probably, phenol and *o*-cresol were cometabolically degraded with acetate. Additionally, no sign of inhibitory effect was detected in the experiments with 8 mg COD l^{-1} of phenol and *o*-cresol because the OC and OUR_{MAX} were 33 and 54% higher in test 4 than in test 1, respectively.

These results showed that the activated sludge from the pilot plant was capable to biodegrade the most recalcitrant intermediates of o-cresol CWAO after more than 125 days of continuous operation in the pilot scale WWTP. This fact could be mainly due to the increase in the capacity of the activated sludge to co-metabolise phenolic compounds with readily biodegradable intermediates or due to the growth of microorganisms capable to use phenolic compounds as substrate.

Therefore, this work demonstrates that an AC/CWAO coupled with a biological municipal WWTP is a feasible treatment for wastewater containing o-cresol in terms of efficiency, operation and legislation. Also, the respirometric procedure is a useful screening method to determine the effect of each AC/CWAO intermediate over an activated sludge and it can help to decide the best way for coupling both treatments.

V.4. Conclusions

An AC/CWAO process coupled with a biological municipal WWTP is a feasible treatment for a high-strength o-cresol wastewater.

The proposed respirometric procedure was a useful screening method to determine the effect of AC/CWAO intermediates on an activated sludge and it allowed classifying them into: readily biodegradable, inert, toxic or inhibitory.

Hydroquinone and p-benzoquinone were the most toxic AC/CWAO intermediates for the aerobic biological treatment but its toxic effect decreased after 125 days of continuous operation in a pilot scale WWTP with the AC/CWAO effluent as a part of the total influent.

The pilot scale municipal WWTP was capable to treat an influent with a 30% of COD coming from AC/CWAO effluent with a high OLR (0.59 mg COD mg-1 VSS d-1), a high COD removal (98%) and a good settleability.

V.5. Acknowledgements

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CHAPTER VI. WAO TESTS AND COMPARISON WITH CWAO TESTS IN TERM OF BIODEGRADABILITY

The results appearing in this chapter have been obtained during the two research stays performed in the Chemical Engineering and Analytical Sciences Department at University of Manchester under the supervision of Prof. Metcalfe. Some parts of the material presented in this chapter has been used in the communication "Phenol wastewater remediation: AOP's coupled to a biological treatment" presented in the 4th Conference on Oxidation Technologies for Water and Wastewater Treatment, held in Goslar, Germany, from May 15th to 17th, 2006.

Outlook

In this chapter, Wet Air Oxidation (WAO) was investigated as a suitable precursor for the biological treatment of industrial wastewaters that contained phenol, o-cresol or 2-chlorophenol. Two hours WAO semi-batch experiments were conducted at 2 and 9 bar of oxygen partial pressure (P_{O2}) and at 215, 240 and 265ºC. The influence of hydroxyl-, methyl- and chloride- substituents on the oxidation mechanism of aromatic compounds was established. The selectivity to the production of carbon dioxide was considerable with total organic carbon (TOC) abatement between 11% and 86%. The readily biodegradable COD fraction ($\%COD_{RB}$) of the WAO effluents was found by respirometric techniques. The maximum $\%COD_{RB}$ was 24% for phenol WAO at 265ºC and 9 bar of P_{O2}, 10% for o-cresol WAO at 265ºC and 9 bar of P_{O2} and 19% for 2-chlorophenol WAO at 215ºC and 2 bar of P_{O2}. These results allows comparing whether or not the WAO effluents were suitable for a conventional activated sludge plant inoculated with non adapted culture. Also, the results of this chapter will be compared to those obtained for the same model compounds using Catalytic WAO with activated carbon, as explained in chapters III and IV. This comparison will allow establishing whether or not the WAO effluents are less biodegradable or has more refractory intermediates than CWAO effluents.

VI.1. Introduction

In the world's consumer-based economy, the chemistry plays an essential role in our attempt to feed world's population, to find new sources of energy, to maintain the humankind, to improve health, to eliminate sickness, to provide substitutes for rare raw materials, to design necessary materials for new information and communication technologies and to monitor and protect our environment. In that way, over fourteen million different molecular compounds have been synthesised during the last century and about one hundred thousand can be found on the market. Only a small fraction of them are found in nature [13]. This increasing design of new materials has produced new sources of pollution which have often turned to be toxic, persistent and difficult to eliminate from the aquatic systems.

A critical issue associated to this rapid industrial and technological development is the sustainable wastewater management. The environmental concern is nowadays expressed by more and more stringent governmental regulations imposing lower pollutant discharge limits. So, for many industrial sectors, pollution prevention, waste minimisation and reuse are being increasingly integrated in their environmental policies. Thus, the challenges faced by chemical and related industries are to design efficient and cheap remediation processes and minimisation strategies for the water pollution problems.

There are several technologies available for removing both organic and inorganic pollutants from industrial process waters and wastewaters [161]. Wet air oxidation (WAO) is a well-established technique for wastewater treatment, particularly toxic and highly organic wastewater [37, 161]. But, WAO cannot fully mineralise pollutants without employing temperatures higher than 275°C and/or a catalyst, thus converting in CWAO; therefore, WAO is frequently used as a pre-treatment to biological treatment processes [161, 162].

The present chapter aims to demonstrate the feasibility of using WAO as pre-treatment for biological remediation of industrial wastewaters containing phenolic compounds such as phenol, o-cresol or 2-chlorophenol. Two hours WAO semi-batch experiments were conducted at 2 and 9 bar of oxygen partial pressure (P_{O2}) and at 215, 240 and 265ºC. The results of this chapter will be compared to those obtained for the same model compounds, but using Catalytic WAO with activated carbon as pre-treatment technique. This comparison will allow establishing whether or not the WAO effluents are less biodegradable or has more refractory intermediates than CWAO effluents.

VI.2. Experimental

VI.2.1. Materials

Aldrich provided analytical grade phenol, o-cresol and 2-chlorophenol. Table III.7 summarises the molecular weight, pKa, solubility and purity of the model compounds. Deionised water was used to prepare all the solutions. HPLC (high performance liquid chromatography) grade methanol (Aldrich) and ultra-pure water (ELGA SP1 195 R.O.) were used to prepare HPLC mobile phases. The synthetic air used as oxidant had a purity of 99.995% (BOC gases, UK).

Phenol and o-cresol feed concentrations were taken as 5 g l^{-1}, whereas for 2-chlorophenol, the feed concentration was taken as 0.5 g l^{-1} to avoid corrosion problems in the reactor vessel [163]. In terms of Chemical Oxygen Demand (COD), the initial feed concentrations were 10.8 g COD l^{-1} for phenol, 9.5 g COD l^{-1} for o-cresol and 0.75 g COD l^{-1} for 2-chlorophenol.

VI.2.2. Experimental set-up and procedures for WAO experiments

WAO experiments were done in a 0.5-litre working volume stainless steel high-pressure reactor (Autoclave engineers, USA). A schematic diagram of the WAO reactor used in this work is in Figure VI.34. In each semi-batch experiment, 500 ml of the solution were introduced into the reactor. Then, the reactor was heated at the desired temperature with air-free nitrogen. As soon as the set temperature was reached, defined as time zero, air was continuously fed into the reactor while being stirred at 1000 rpm. Samples were withdrawn every 30 minutes. After the total reaction time (120 min), the airflow was shut off and the reactor was depressurised (through relief valve) to a pressure above the vapour pressure at the reaction temperature. Most of the air was removed stopping the oxidation while no evaporation of liquid phase occurred. As soon as the temperature dropped to ambient conditions, the autoclave was opened and the reactor content was collected for analysis. Each sample was analysed to determine model compound destruction (X), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and biodegradability enhancement as readily biodegradable COD percentage (%COD_{RB}). Experiments were done at 215ºC, 240ºC and 265°C and total pressure from 30 to 93 bar depending on the oxygen partial pressure (P_{O2}) selected for the experiment (2 or 9 bar).

The same experiment was conducted twice to check the reproducibility of results and the match (within ±5%) between successive experiments was excellent. The data reported in the paper are the arithmetic average of the results derived from repeated WAO experiments.

Sample concentrations of substituted phenols, quinone-like intermediates (catechol, hydroquinone and p-benzoquinone) and acidic intermediates such as oxalic, formic, malonic, acetic, maleic (and its isomer fumaric acid), succinic, 4-hydroxybenzoic (4-HB) and salicylic (2-HB) acids were determined by HPLC (Varian Prostar). The analysis was done using a C18 reverse phase column (Thermo-ThermoHypersil ODS) and a mixture of ultra-pure water (phase A) and methanol (phase B). The gradient started from 100 % of A and progressively changes to 50:50 v/v of A:B in 25 minutes, then it remained isocratic until minute 37. Both mobile phases were acidified to pH equal to 2 with concentrated sulphuric acid. The intermediates considered for HPLC calibration were in part reported in the reaction pathway described by Devlin and Harris [88] for phenol WAO.

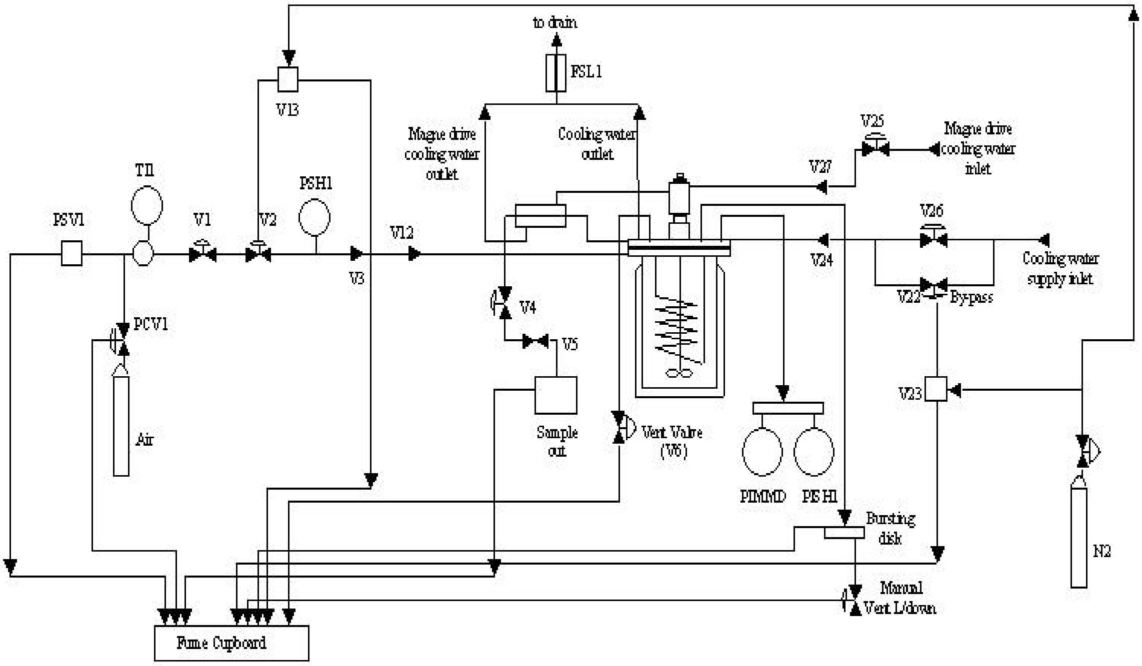

Figure VI.34. Schematic diagram of WAO used in this study.

COD was measured with the standard method 5220D [87]. TOC was quantified with a Shimadzu TOC-V CSH analyser based on combustion and subsequent non-dispersive infrared (NDIR) CO_2 detector. The CO_2 selectivity was inferred from mass balance between the initial and final TOC values in the experimental samples.

As usual, the results are compared in terms of conversion, i. e. model compound destruction. The general expression used is:

$$X(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \cdot 100 \qquad \text{Equation VI.19}$$

where C_0 is the inlet concentration and C_e is the concentration in the effluent. Equation VI.26 can also be used to calculate TOC abatement (X_{TOC}) in a similar way.

A complete scheme of the WAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [86, 162, 164]. Several pictures of the equipment used to do the WAO tests can be found in Annex I.

VI.2.3. Experimental set-up and procedure for respirometric tests

A respirometer was used to measure the biodegradability enhancement. A respirometer is a small biological reactor for the measurement of the Oxygen Uptake Rate (OUR). The respirometer used in this study corresponds to a LFS type [68], in which dissolved oxygen (S_O) is measured in the liquid-phase (L), which is static (S) and the air flows continuously (F).

The air was feed through a pressure manoreductor and through a gas rotameter (AAlborg 150 mm with micro-regulation valve) to ensure constant airflow. An air diffuser dispersed the air in micro-bubbles before entering to the respiration vessel (1 litre). The vessel was magnetically stirred to prevent dead zones in air diffusion. The pH, S_O and temperature were measured with pH and S_O probes (VWR Sentix 81 and Cellox 325) which were monitored with a PC using a multiparametric module (VWR Inolab 3). The respirometer was immersed in a temperature bath, at 30.5±0.5 ºC and the pH inside the respirometer was maintained at 7.5±0.5. The respirometer was inoculated with biomass from the municipal WWTP of Tarragona (Catalonia, Spain). The determination of Volatile Suspended Solids (VSS) was done according to the Standard Methods for the Examination of Water and Wastewater [87]. The values of VSS were 3400 ± 320 mg $VSS \cdot l^{-1}$.

Biodegradability tests consist in the addition of a substrate pulse of 20 COD mg l^{-1} to the biomass inside the respirometer. Then, OUR profile is obtained solving the S_O balance in the liquid phase of the respirometer. The biodegradation parameters used to compare OUR profiles obtained in each experiment are the area under the OUR profile or oxygen consumption (OC) and the maximum value of the OUR profile (OUR_{MAX}). More information about the OUR calculation can be found elsewhere [68, 71].

All the respirometric data presented in this chapter correspond to the arithmetic average of the results derived from two equal experiments. The reproducibility of the results and the match (within ±10%) between successive experiments was excellent.

During the discussion, the WAO conditions will use the following nomenclature: 215-2 will refer to 215ºC and 2 bar of P_{O2}, 265-9 equals to 265ºC and 9 bar of P_{O2} and so on.

VI.3. Results and Discussion

The results and discussion are divided into two sections. In the first, the WAO performance is discussed by means of X and X_{TOC}. Also, the reactivity order, the detected intermediates and the reaction mechanisms are examined. In the second section, the determination of the biodegradability of WAO effluents is presented.

VI.3.1. Model Compound Disappearance and Intermediates Distribution.

Figure VI.33 shows the X, X_{TOC} and pH profiles for phenol, o-cresol and 2-chlorophenol tests at the four conditions of temperature and P_{O2} tested. As example, at the end of the tests at 265-9, X are between 90 and 100% for all compounds. At 265-2, X is close to 98% for 2-chlorophenol, 95% for o-cresol and 26 % for phenol. At 240-2, X is close to 98% for 2-chlorophenol, 61% for o-cresol and 26 % for phenol. Finally, at 215-2, X is close to 98% for 2-chlorophenol, 58% for o-cresol and 21 % for phenol.

As expected, X_{TOC} is lower than the respective X because of the presence of partially oxidised products. It should be pointed out that the higher the difference between X and X_{TOC}, the higher the amount of partially oxidised products in the liquid effluent and the lower the selectivity to CO_2. For instance, the differences between X and X_{TOC} at the end of the tests at 265-9 are 17% for phenol, 15% for o-cresol, and 12% for 2-chlorophenol. At the end of the tests, as far as X is concerned, the experimental reactivity order is 2-chlorophenol ≈ o-cresol > phenol.

In order to compare the degradation extent between WAO and CWAO, the X and X_{TOC} of both processes are presented in Table VI.25.

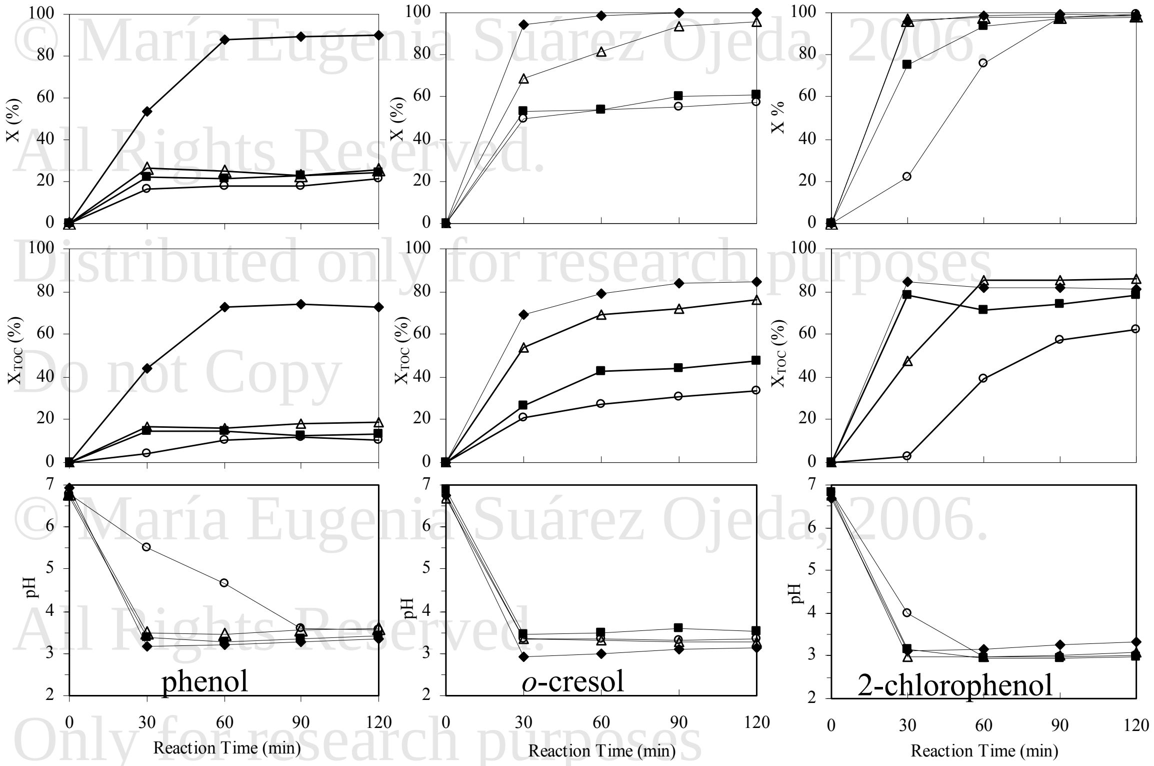

Figure VI.35. Conversion (1st row), TOC abatement (2nd row) and pH (3rd row) profiles for phenol (left), o-cresol (centre) and 2-chlorophenol (right) at different conditions. Symbols indicate experimental data {(♦) 265-9, (Δ) 265-2, (■) 240-2, (○) 215-2}. Lines only show tendencies.

Compared to the results obtained with CWAO (Table VI.25) several trends can be drawn. First, for 2-chlorophenol the X o X_{TOC} obtained with WAO are always higher than those obtained with CWAO. In the case of phenol, in general the X or X_{TOC} obtained with CWAO are higher than those achieved with WAO, however, with WAO at 265-9, the attained X or X_{TOC} are the highest one between both oxidation processes for phenol.

Table VI.25. X and X_{TOC} in WAO and CWAO.

WAO								
T(ºC)-P_{O2}(bar)	215-2		240-2		265-2		265-9	
Compound	X	X_{TOC}	X	X_{TOC}	X	X_{TOC}	X	X_{TOC}
phenol	21	12	24	13	26	14	90	73
o-cresol	57	33	61	47	95	76	100	85
2-chlrophenol	99	62	98	79	97	81	99	86
CWAO								
T(ºC)-P_{O2}(bar)	140-2		140-9		160-2		160-9	
Compound	X	X_{TOC}	X	X_{TOC}	X	X_{TOC}	X	X_{TOC}
phenol	45	21	58	32	78	62	80	52
o-cresol	33	14	97	40	83	47	90	46
2-chlrophenol	55	47	60	49	75	69	80	56

Finally, for o-cresol, the X or X_{TOC} varies depending on the process. For instance, the highest X is obtained with CWAO at 140-9 and 160-9 and at 265-9 and 265-2 in WAO. However in the case of X_{TOC}, with WAO at 265-2 and 265-9, the X_{TOC} is higher than either X_{TOC} obtained with CWAO, therefore the mineralization degree obtained with WAO at 265-2 and 265-9 is higher that with CWAO at 140-9 and 160-9.

The phenols oxidation mechanism is very complex and is not yet fully understood. It has been reported that the WAO of phenol and some substituted phenols in aqueous solution by molecular oxygen is an electrophilic reaction that follows a heterogeneous-homogeneous free radical chain mechanism, where the limiting step is the reaction between the aryloxy radical and oxygen [96]. For the free radical mechanism, the phenol oxidation must be characterised by an induction period followed by a fast reaction phase typical of radical mechanism. However, in this study no induction period was observed, probably because appears before 30 min, when the first sample is taken.

The facility in which phenols form aryloxy radicals is related to the Half-wave oxidation potentials (HWP); the lower the HWP, the easier oxidation is [97]. As Table III.9 shows, the HWP of the model compounds are ordered as follows: o-cresol ≥ 2-chlorophenol > phenol. Therefore, for a free radical mechanism, the reactivity order should follow the same order. Also, as explained by Joglekar et al. [96], the phenols oxidation by electrophilic substitution increases as the steric crowding in ortho- positions and the electron-releasing properties of substituents in ortho- and para- positions increase. Hence, the reactivity order found in this study is close to the reactivity order found by Joglekar et al. [96] and to the HWP order discussed earlier.

Turning to pH, at the start the pH has the value of the initial solution according to the pKa values of each model compound (Table III.7). Then the pH begins to decrease, which is caused by the formation of organic acids as oxidation by-products, as confirmed by the HPLC analysis.

The distribution of major identified intermediates obtained for phenol, o-cresol and 2-chlorophenol WAO are shown in Figure VI.37, Figure VI.38 and Figure VI.39, accordingly.

In the case of phenol samples (Figure VI.37), the main partial oxidation products were light carboxylic acids such as oxalic, acetic and succinic acids in concentration between 110 and 665 mg l^{-1}. Malonic, maleic, fumaric (maleic acid isomer), 4-HB and 2-HB acids were detected in amounts between 5 mg l^{-1} and 100 mg l^{-1}. Finally, hydroquinone and catechol were detected in concentrations up to 350 mg l^{-1}, whereas p-benzoquinone was detected in concentration as low as 8 mg l^{-1}. No other possible intermediates were detected.

The presence of 4-HB and 2-HB suggest a reaction pathway where either phenol or dihydric-phenols (hydroquinone and catechol) can be destroyed via two routes. The first one leading to the formation of benzoquinones seems to govern the reaction. The second route could proceed through the reaction of phenol with malonic acid to form 4-HB and/or 2-HB and acetic acid as Figure VI.36 shows. To the best of our knowledge this second route has not even reported in the un-catalysed oxidation of phenol. Only two works reported the presence of 4-HB as reaction intermediate but, for CWAO of phenol with activated carbon as catalyst [131, 165].

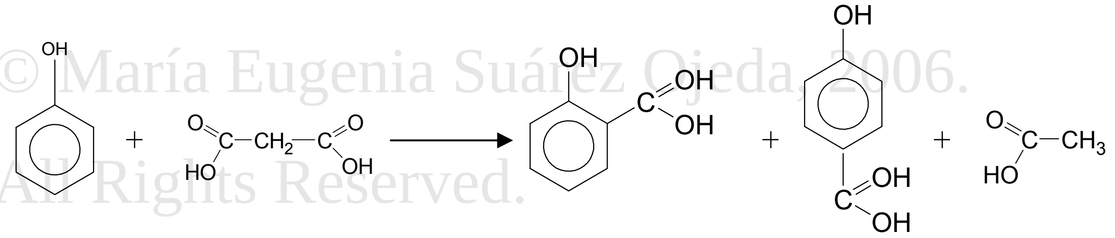

Figure VI.36. Reaction network proposed for 4-HB/2-HB formation from WAO of phenol without catalyst.

As can be seen from Figure VI.37, oxalic and acetic acids accumulate with the reaction time, which clearly indicates the refractoriness of these compounds to further oxidation. The other acids, in general, increase their concentration during the first 60 minutes and later a decrease in their concentration in observed.

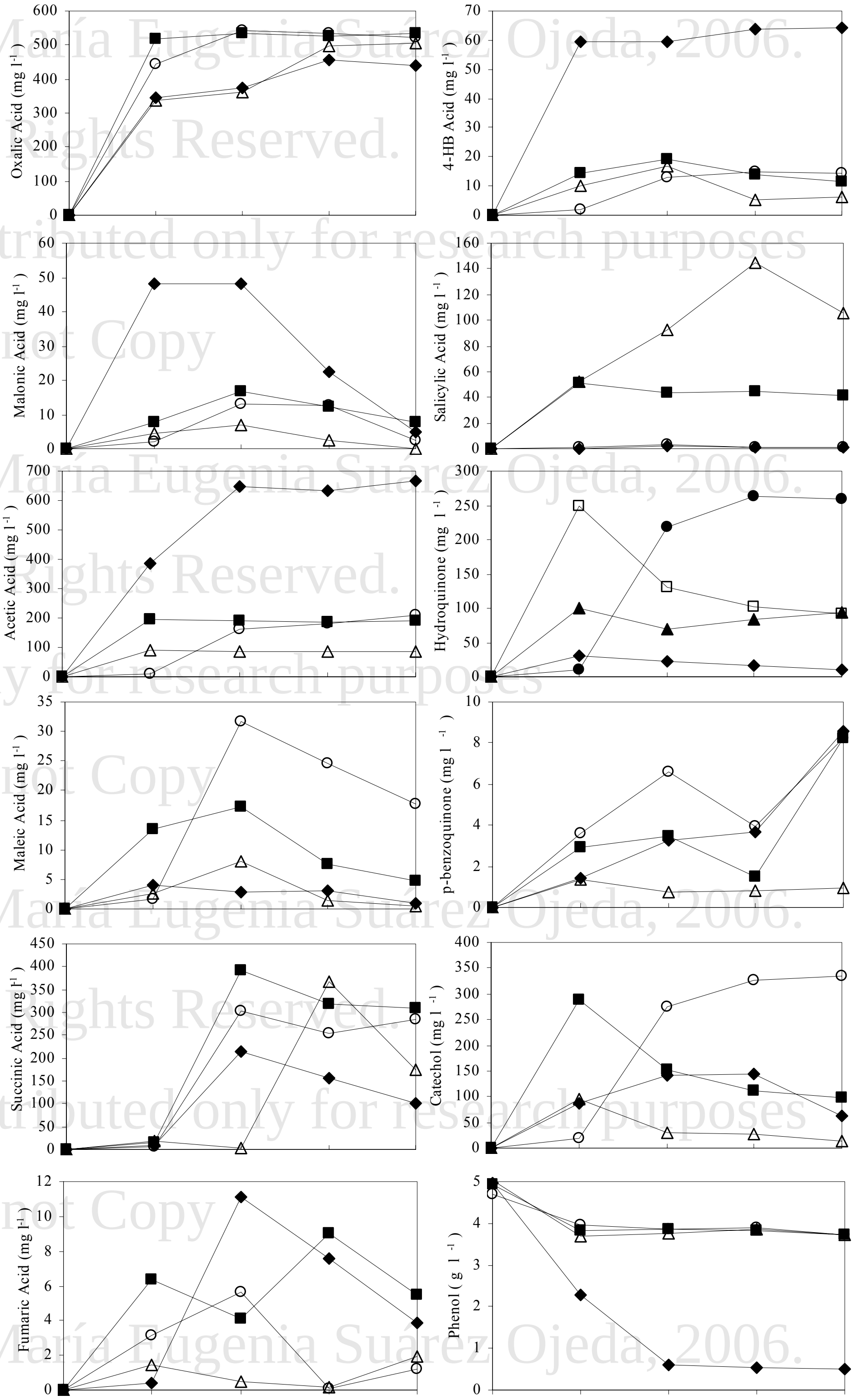

Figure VI.37. Distribution of major identified intermediates during WAO of phenol at the temperatures and the pressures tested in this study. Symbols indicate experimental data {(♦) 265-9, (Δ) 265-2, (■) 240-2, (○) 215-2}. Lines only show tendencies.

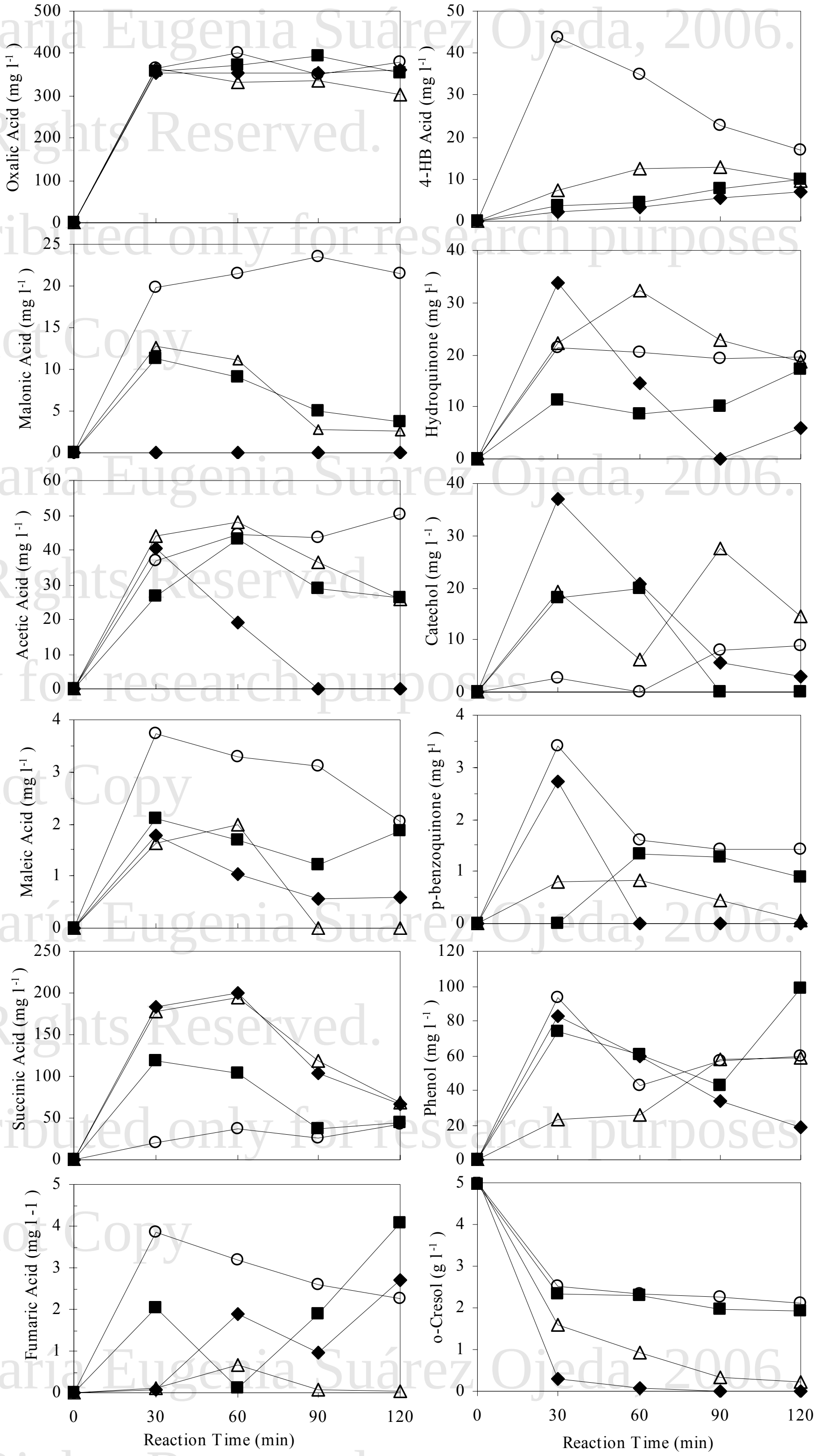

Figure VI.38. Distribution of major identified intermediates during WAO of o-cresol at the temperatures and the pressures tested in this study. Symbols indicate experimental data {(♦) 265-9, (Δ) 265-2, (■) 240-2, (○) 215-2}. Lines only show tendencies.

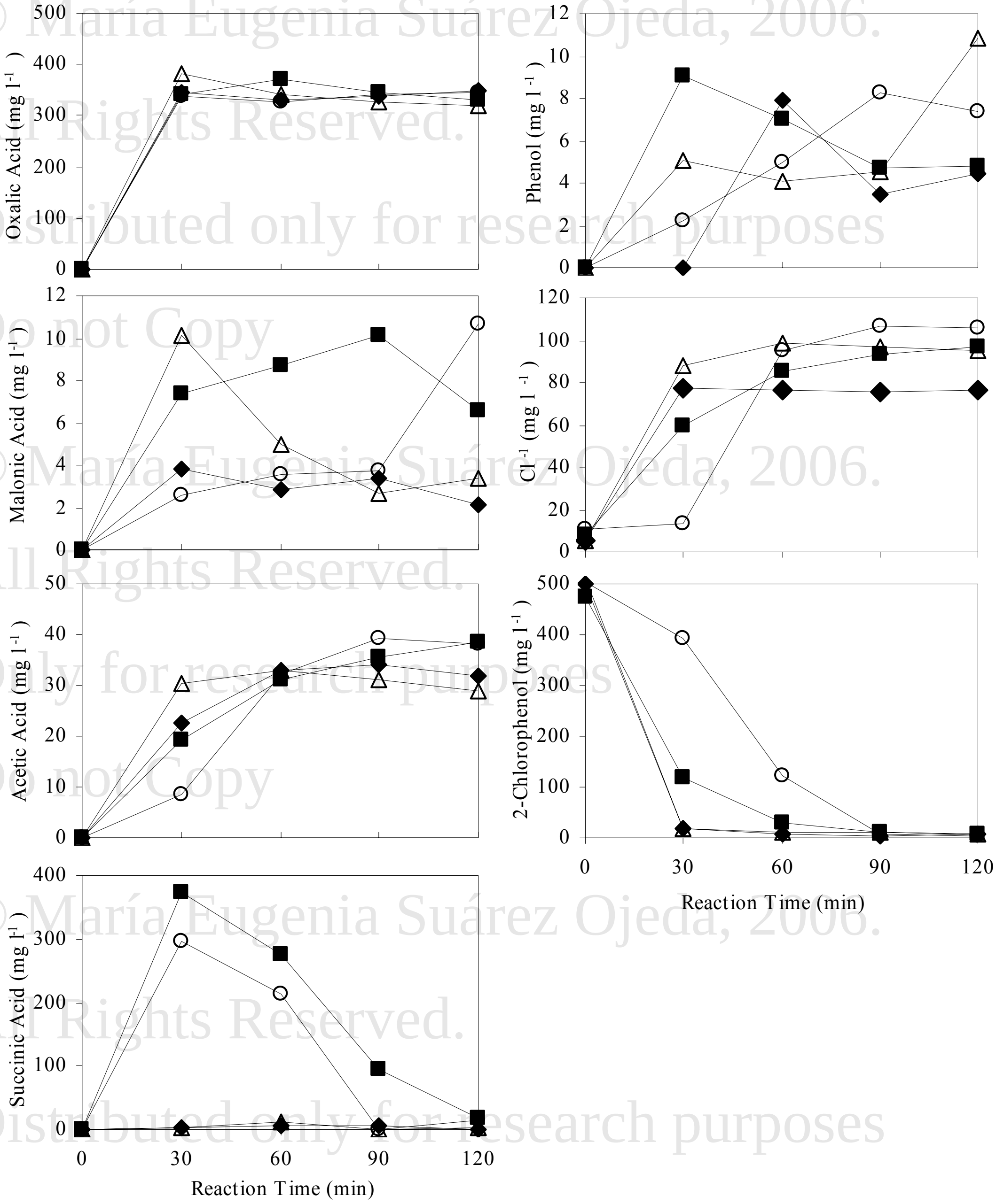

Figure VI.39. Distribution of major identified intermediates during WAO of 2-chlorophenol at the temperatures and the pressures tested in this study. Symbols indicate experimental data {(♦) 265-9, (Δ) 265-2, (■) 240-2, (○) 215-2}. Lines only show tendencies.

This behaviour of concentration profiles is typically found in a consecutive reaction model. Also, it can be noted from Figure VI.37 that hydroquinone and catechol profiles are very similar in all the conditions, which could indicate that they are equivalent reaction pathways. Without the exception of 215-2 profiles, both hydroquinone and catechol increase their concentration in the first 30 min and then begin to decrease being further oxidised to light carboxylic acids.

For o-cresol samples (Figure VI.38), oxalic and succinic acids were the main light carboxylic acids, appearing in concentrations up to 400 mg l^{-1}. Other acids like malonic, acetic, maleic, fumaric and 4-HB acids were detected in concentrations below 50 mg l^{-1}. Neither formic acid nor 2-HB acid were detected. The quinone-like intermediates, such as hydroquinone and catechol, were measured in amounts below 35 mg l^{-1} whereas p-benzoquinone concentrations were found almost at trace levels. Finally phenol was detected as reaction intermediate of o-cresol WAO in amounts up to 100 mg l^{-1}. The absence of 2-HB as intermediate in o-cresol WAO suggest that direct oxidation of the methyl-side chain, which could lead to 2-HB formation, does not occur in the tested conditions.

Finally, in the case of 2-chlorophenol samples (Figure VI.39), oxalic and succinic acids were detected again as main light carboxylic acids in concentrations up to 350 mg l^{-1}. The other acidic intermediates detected were malonic and acetic acids, but in amounts below 40 mg l^{-1}. Hydroquinone, catechol and p-benzoquinone were not detected and phenol was measured in concentrations as low as 10 mg l^{-1}. In turn, chloride ions were detected in amounts between 5 and 100 mg l^{-1}. If total dechlorination occurs and no other chlorinated intermediates are formed, the maximum concentration of free chloride ions should be 140 mg l^{-1}. These results indicate that other non-identified chlorinated intermediates should be in the effluents from 2-chlorophenol WAO, as the mass chloride ions concentration is below the maximum expected.

VI.3.2. WAO effluents biodegradability

Biodegradability respirometric tests were conducted with each WAO effluent following the procedure explained in chapter V. Biodegradability of WAO effluents will be compared to those obtained for the same model compounds, but using Catalytic WAO with activated carbon (AC), as explained in chapters IV and V, in order to establish whether or not the WAO effluents are less biodegradable or has more refractory intermediates than CWAO effluents. Also, the results will be explained using the biodegradability information extracted from the data corresponding to each major intermediate presented in chapter V with the same non-acclimatised biomass and the same experimental procedure.

As previously established, the readily biodegradable intermediates are: fumaric, propionic, acetic, succinic, formic and glyoxilic acids. Also, other CWAO intermediates were classified as inert intermediates that seemed to be non-readily biodegradable but they did not show any toxic or inhibitory effect (oxalic, maleic, malonic 4-HB and 2-HB acids and catechol, hydroquinone and *p*-benzoquinone at 1 mg COD l^{-1}). Additionally, other CWAO intermediates were found to have a negative effect on the OC and the OUR_{MAX} of the control substrate, indicating a toxic or inhibitory behaviour (catechol at 4 mg COD l^{-1}) or toxic (hydroquinone and *p*-benzoquinone at 4 mg COD l^{-1}).

Figure VI.40a shows the comparison in terms of $\%COD_{RB}$ obtained for phenol oxidation in the semi-batch WAO experiments (at 120 min of reaction time) and in the continuous CWAO experiments at several temperatures and P_{O2}, from the most severe condition (265-9) to the lowest one (140-2). Figure VI.40b and in Figure VI.40c display the same information for o-cresol and 2-chlorophenol, respectively. Data of CWAO are taken from chapter V.

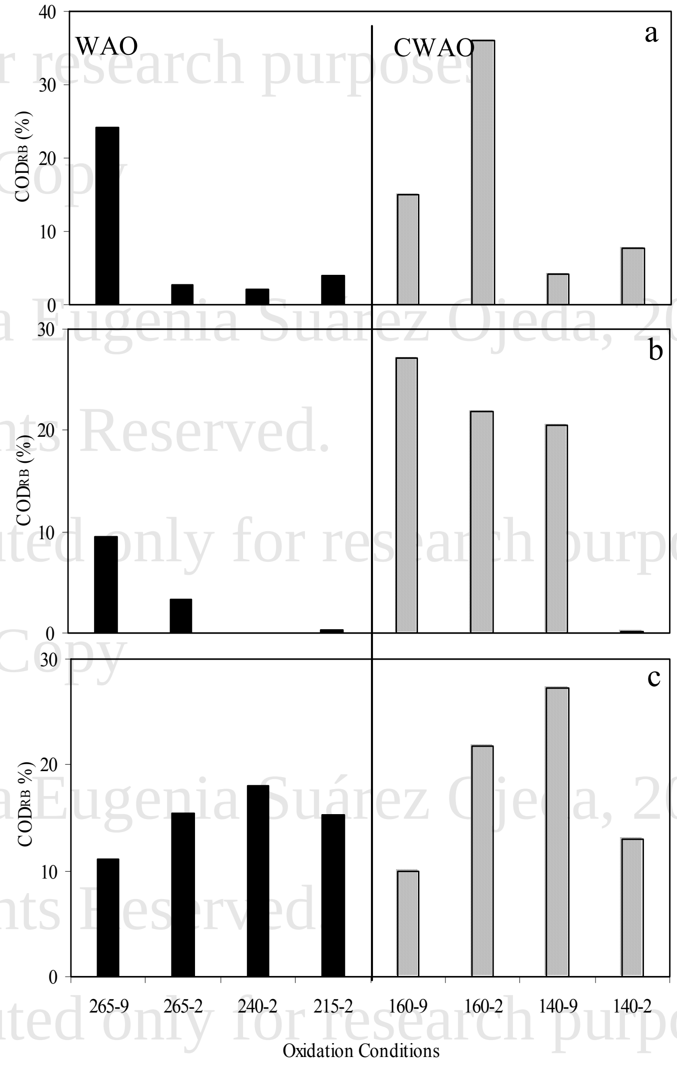

Figure VI.40. Readily biodegradable COD fraction of phenol (a), o-cresol (b) and 2-chlorophenol (c) effluents from WAO and CWAO.

For phenol WAO effluents (Figure VI.40a), there was a very low $\%COD_{RB}$ at 215-2, 240-2 and 265-2, probably because the low concentration of carboxylic acids and the high remaining phenol concentration. The maximum $\%COD_{RB}$ (24%) for WAO tests occurred at 265-9. At this condition, the sum in concentration of readily biodegradable acids showed a maximum (Figure VI.37), representing 27% of the total COD, whereas the sum in concentration of possible toxic/inhibitory intermediates (catechol, hydroquinone and *p*-benzoquinone) showed a low value (5% of the total COD). Comparing the phenol WAO results with those obtained with phenol in CWAO (Figure VI.40), in general, the $\%COD_{RB}$ is higher in CWAO than in WAO. Those differences in biodegradability could be explained by the differences in the intermediate distribution in both treatments. In WAO the readily biodegradable intermediates were in lower proportion and the possible toxic/inhibitory intermediates were in higher proportion than in CWAO, which explains the better biodegradability enhancement, when using CWAO.

Similar trends can be drawn for o-cresol WAO effluents. There was no biodegradability at 215-2 and 240-2 because the remaining *o*-cresol concentration was the highest and the readily biodegradable intermediates (acetic, succinic and fumaric) concentrations were very low (Figure VI.38). For the rest of conditions, the $\%COD_{RB}$ was 10% and 3% at 265-9 and 265-2, accordingly. At 265-9, from Figure VI.38, the proportion of readily biodegradable acids is not the highest one, but the non-identified intermediates (data not shown) lie in the retention times of carboxylic acids, probably being other type of readily biodegradable intermediates. Comparing the o-cresol WAO results with those obtained with o-cresol in CWAO (Figure VI.40), in general, the $\%COD_{RB}$ is higher again in CWAO than in WAO. These differences in the biodegradability enhancement could be explained by the difference in the intermediates distribution between both treatments (already explained for phenol). Nevertheless, it could be also related to the fact that TOC abatement is higher in o-cresol WAO than in CWAO treatment, leaving the WAO effluents without intermediates that could be further consumed by the microorganisms in the respirometry tests.

Finally, for 2-chlorophenol WAO (Figure VI.40) the $\%COD_{RB}$ obtained were comparable to those obtained with CWAO, ranging from 10 to 27%. Hence, both WAO and AC/CWAO are suitable technologies for 2-chlorophenol treatment, in terms of biodegradability enhancement and X, therefore the final selection of the treatment should be based on technical and economic feasibility or availability.

VI.4. Conclusions

Several WAO tests were performed with 2-chlorophenol, phenol, and o-cresol, as model compounds in order to establish wheater or not the WAO effluents were suitable for a WWTP. Conversions were between 21 and 100%. As far as X is concerned, the experimental reactivity order was 2-chlorophenol ≈ o-cresol > phenol.

The presence of 4-HB and 2-HB suggest the occurrence of a side pathway of phenol removal through the condensation of phenol with malonic acid. However, this route is not dominating and the classic one still seems to be the main degradation way. In the case of o-cresol, the absence of 2-HB as intermediate suggest that direct oxidation of the methyl-side chain, did not occur in our experiments.

Finally, although 2-chlorophenol completely disappears, the chloride concentration is lower than the maximum expected, indicating that other non-identified chlorinated intermediates should be in the effluents from 2-chlorophenol WAO. Also, phenol concentrations were below 10 mg l^{-1}, suggesting an alternative reaction pathway for 2-chlorophenol degradation.

The differences in biodegradability between WAO and CWAO effluents could be explained by the differences in the intermediate distribution in both treatments. In general, in WAO the readily biodegradable intermediates were in lower proportion and the possible toxic/inhibitory intermediates were in higher concentration than in CWAO, which renders a better biodegradability enhancement of the CWAO treatment.

However, for 2-chlorophenol, both WAO and AC/CWAO are suitable technologies, in terms of biodegradability enhancement and therefore the final selection of the treatment should be based on technical and economic feasibility or availability.

At present, research focuses on establishing the kinetic model of substituted phenol in WAO, including both the intermediates and biodegradability enhancement prediction.

VI.5. Acknowledgements

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School, University of Manchester) and Dr. Y. Muñoz (Physicochemical Department, Universidad de Concepción, Chile) for their useful discussions.

CHAPTER VII. CATALYTIC AND NON-CATALYTIC WET AIR OXIDATION OF SODIUM DODECYLBENZENE SULFONATE: KINETICS AND BIODEGRADABILITY ENHANCEMENT

The material of this chapter had been done in collaboration with Prof. Metcalfe and his PhD student J. Kim, so all the data of WAO experiments were done by them. Some parts of the material presented in this chapter has been used in the oral communication "Catalytic and Non-catalytic Wet Air Oxidation of Sodium Dodecylbenzene Sulfonate: Kinetics and Biodegradability Enhancement" presented in the 5th European Meeting on Chemical Industry and Environment (EMChIE 2006), held in Vienna, Austria, from May 3rd to 5th, 2006.

Outlook

Sodium dodecylbenzene sulfonate (DBS), a member of the linear alkylbenzene sulfonates (LAS) family, is worldwide used as detergent, as dispersant, and as anionic surfactant. Although LAS has successfully treated at low concentrations in conventional aerobic biological treatments, LAS can be categorized as a toxic organic compound. LAS have biological inhibitory effect at high concentration, such as those of detergent manufacturing wastewater. Among that, other problems are also observed, such as foaming, decreased oxygen mass transfer in the aeration basin and poor sludge settling. Therefore, a more suitable treatment for concentrated LAS in aqueous phase is required.

With this goal, Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO) were investigated as suitable precursors for the biological treatment of industrial wastewater containing DBS. Two hours WAO semi-batch experiments were conducted at 15 bar of oxygen partial pressure (P_{O2}) and at 180, 200 and 220ºC. It was found that the highest temperature provides appreciable Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) abatement of about 42 and 47%, correspondingly. Based on the main identified intermediates (acetic acid and sulfobenzoic acid) a reaction pathway for DBS in WAO is proposed. In the case of CWAO experiments, seventy-two hours tests were done in a fixed bed reactor in continuous trickle flow regime, using a commercial activated carbon (AC) as catalyst. The temperature and P_{O2} were 140ºC-160ºC and 2-9 bar, respectively. The influence of the operating conditions on the DBS oxidation, the occurrence of oxidative coupling reactions over the AC, and the catalytic activity (in terms of substrate removal) were established. The results show that the AC without any supported active metal behaves bi-functional as adsorbent and catalyst, giving TOC conversions up to 52% at 160ºC and 2 bar of P_{O2}, which were comparable than the obtained in WAO experiments. Respirometric tests were completed before and after CWAO and to the main intermediates identified through the CWAO oxidation route. Then, the readily biodegradable COD fraction (%COD_{RB}) of the CWAO was found. Taking into account these results it was possible to compare whether or not the CWAO or WAO effluents were suitable for a municipal biological WWTP with non-acclimatised biomass.

VII.1. Introduction

Sodium dodecylbenzene sulfonate (DBS), a member of the linear alkylbenzene sulfonates (LAS) family [35, 166] is used as detergent, as dispersant, and as anionic surfactant. Homologous series of LAS are mainly used in dentifrice products, in hair shampoos, and in emulsion polymerisation. The rest is either used in special cosmetic formulations, e.g. for bubble baths and hair bleaches, or as a fine chemical, e.g. as denaturing agent in gel electrophoresis. Also, technical grade LAS is used as detergent in dish-washing products, as additive for plastics and lattices, and in paints and lacquers.

Besides, the high quantities that are eventually rejected in the environment, LAS are a recognised toxic substance listed in the 2000 OECD List of High Production Volume Chemicals [109]. For instance, in microbial toxicity studies with Daphnia Magna exposed for 48 hours to LAS, the EC_{50} value is 6.8 mg l^{-1} [167]. Although LAS in wastewater has been successfully treated by conventional biological wastewater treatment plant (WWTP) at low concentrations [168, 169], it has a biological inhibitory effect at high concentration such as those from detergent manufacturing wastewater streams which can have a COD of up to 50 g l^{-1} [86]. Highly concentrated LAS wastewater, results also in others problems in the WWTP, such as foaming and oxygen mass transfer limitations in the aeration basin and poor sludge settling, making necessary the LAS neutralization and increased retention times. Moreover, a large fraction of LAS are adsorbed into the sludge, so LAS is eliminated from the WWTP during the removal of the excess sludge instead of being a true biodegradation [169, 170]. In recent years, Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO) have been increasingly focused on the treatment of biologically refractory organic compounds. Unfortunately, the high temperatures and pressures used in WAO requires expensive reactors making the overall treatment expensive [171, 172] and in the case of CWAO, the lack of both active and stable catalysts is a serious drawback, which prevents a wider industrial implementation [37, 73 and 74].

This study aims to compare both WAO and CWAO as precursors for the biological treatment of industrial wastewater containing DBS. First, several WAO tests were performed in order to understand the reaction pathway and identify the major intermediates occurring during WAO subjected to modifications in the temperature and the residence time as the major dominant factors in the oxidation. Second, several CWAO test using activate carbon (AC) as catalyst were performed in order to reduce the temperature and pressure and to control the reaction intermediates with the aim of producing a more biodegradable effluent than in WAO. The AC performance was tested for 5 days so that the evolution of the catalytic activity could be continuously checked. The used AC were further characterised to highlight the role of AC into the DBS reaction mechanism. Finally, the biodegradability enhancement between both processes was compared by using respirometry to get the biodegradability of each CWAO effluent and by using the intermediates distribution of WAO effluents.

VII.2. Experimental

VII.2.1. Materials

Aldrich provided technical grade DBS. Deionised water was used to prepare all the solutions. For prepare high performance liquid chromatography (HPLC) mobile phases, HPLC grade methanol (Aldrich), HPLC grade acetonitrile (Aldrich) and ultra-pure water (Millipore Direct-Q system or ELGA SP1 195 R.O.) were used. The synthetic air used as oxidant in CWAO and WAO experiments has a purity of 99.995% (Carburos Metálicos, Spain and BOC gases, UK).

The AC used as catalyst was purchased by Merck (reference #102518) in the form of 2.5 mm pellets. Prior to use, AC was crushed and sieved. Then, the particle size chosen was 25-50 mesh (0.7-0.3 mm) to minimise both pressure drop and internal mass transfer limitations, according to the work done by Stüber et al. [82]. Later, this fraction was washed to remove all the fines, dried overnight at 105ºC, cooled and stored under inert atmosphere until use. This AC is manufactured from wood and was characterised in a previous study [113] giving a BET surface are of 1481 $m^2 g^{-1}$, a micropore volume of 0.34 $cm^3 g^{-1}$, a BJH cumulative surface area of 304 $m^2 g^{-1}$, a pH_{PZC} of 8.05 and a maximum adsorption capacity for DBS of 1028 $mg_{DBS}\ g_{AC}^{-1}$ at 25ºC (Chapter III).

VII.2.2 Experimental set-up and procedure for WAO

WAO experiments were done in a 0.5-litre working volume stainless steel high-pressure reactor (Autoclave engineers, USA). In a typical semi-batch experiment, 500 ml of the solution with a DBS concentration of 1 g l^{-1} (1.8 g COD l^{-1}) were introduced into the reactor. Then, the reactor was heated at the desired temperature with air-free nitrogen. Experiments were done at temperatures from 180 to 220°C and a P_{O2} of 15 bar was maintained in all the experiments. As soon as the set temperature was reached, defined as time zero, air was continuously fed into the reactor while being stirred at 1000 rpm. After the reaction time, the airflow was shut off and the reactor was depressurised (through relief valve) to a pressure above the vapour pressure at the reaction temperature. Most of the air was removed stopping the oxidation while no evaporation of liquid phase occurred. As soon as the temperature dropped to ambient conditions, the autoclave was opened and the reactor content was collected for analysis to determine remaining Chemical Oxygen Demand (Y_{COD}) and remaining Total Organic Carbon (Y_{TOC}).

VII.2.3. Experimental set-up and procedure for CWAO

CWAO experiments were done in a trickle bed reactor (TBR) in down-flow co-current. The reactor containing the AC packed bed consists of a titanium tube (20 cm long and 1.1 cm i.d.), which is placed in a controlled temperature oven (±1ºC). Typically, 7.0 g of AC was loaded into the reactor. The liquid flow rate was set to give a space time of 0.12 h, i.e. a liquid weight hourly space velocity (WHLV) of 8.2 h^{-1}. Synthetic air was used as oxidant to ensure a P_{O2} of 2 and 9 bar at each temperature. The experiments were run at 140ºC and 160ºC for 72 h. DBS feed concentration was taken as 5 g l^{-1} (9.1 g COD l^{-1}). The air flow rate was kept constant at 2.4 ml STP s^{-1} in standard conditions, which is well beyond the stoichiometric oxygen uptake needed.. Liquid samples were periodically withdrawn and then analysed to determine Y_{COD} and Y_{TOC}.

In both cases, the same experiment WAO or CWAO was conducted twice to check the reproducibility of results. The match (within +5%) between repeated experiments was excellent. The data reported in the paper are the arithmetic average of the results derived from repeated experiments.

VII.2.4. AC characterisation

At the end of the CWAO test, the AC used was carefully collected and dried at 105ºC overnight under an N_2 atmosphere to remove excess water. Then, the AC was divided into three parts. The first one of them (approx. 20 mg) was subjected to Thermogravimetric Analysis (TGA). The analysis was carried in a Thermobalance Perkin-Elmer model TGA7, TCA7. The sample was heated from 100ºC to 900ºC under nitrogen flow at a heating rate of 10ºC min^{-1}. The second part (between 15 and 20 mg) was used to determine textural properties by nitrogen adsorption isotherms at 77 K in a Micromeritics instrument model ASAP 2010. The textural properties such as surface area, micropore volume and cumulative surface area were calculated by applying different model methods i.e. BET, Harkins and Jura t-plot and Barret-Joyer-Halenda (BJH) which are included with the Micromeritics software. Finally, the remaining used AC was dried at 400ºC under nitrogen atmosphere to remove any physisorbed compound. Subsequently, the AC was weighed to measure the weight change (WAC).

VII.2.5. Analytical procedures

Sample concentrations of DBS were immediately determined by HPLC (Agilent 1100 or Varian Prostar). The analysis method was adapted from Matthijs and De Henau [85] and Patterson [86] and was performed with a C18 reverse phase column (Agilent -Hypersil ODS or Thermo-ThermoHypersil ODS), using an acetonitrile-water-sodium perchlorate mobile phase to separate the DBS from its reaction products. Two mobile phases were used. Solution A was a mixture of acetonitrile and water with a proportion of 70:30 v/v whereas solution B was only water. Sodium perchlorate was added to both mobile phases at a concentration of 0.15 M. A flowrate of 1 ml min^{-1} and a wavelength of 225 nm were used. Identification and quantification of several carboxylic acids were done with different methods. 4-sulfobenzoic acid was quantified with two mobile phases at flow rate 1 ml min^{-1}: solution A containing a mixture of acetonitrile and water (20:80 v/v) and solution B containing just water; again sodium perchlorate was added to both mobile phases at a concentration of 0.15 M.

For other acidic intermediates (glyoxilic, oxalic, formic, 4-hydroxybenzoic sulfonic, malonic, acetic, succinic, fumaric, benzene sulfonic and propionic acids), the analysis was done using a mixture of ultra-pure water (phase A) and methanol (phase B). The gradient started from 100 % of A and progressively changes to 50:50 v/v of A:B in 25 minutes, then it remained isocratic until minute 37. Both mobile phases were acidified to pH equal to 1.5 with concentrated sulphuric acid.

COD was measured with the standard method 5220D [87], whereas TOC was quantified with the method 5310B [87]. The CO_2 selectivity was calculated by a mass balance between the initial and final TOC values in the experimental samples.

The results are compared in terms of remaining COD and TOC in the effluents. The general expression used is:

$$Y(\%) = \left(\frac{C_e}{C_0}\right)\cdot 100$$

Equation 20

where C_0 is the inlet concentration and C_e is the concentration in the effluent.

VII.2.6. Experimental set-up and procedure for respirometric tests

A respirometer was used to measure biodegradability enhancement. This respirometer is a small biological reactor for the measurement of the Oxygen Uptake Rate (OUR). The respirometer used in this study corresponds to a LFS type [68], in which dissolved oxygen (S_O) is measured in the liquid-phase (L), which is static (S) and the air flows continuously (F).

The air flows through a pressure manoreductor and through a gas rotameter to ensure constant airflow. The vessel (1 litre) is magnetically stirred to avoid dead zones in air diffusion. The pH, S_O and temperature are measured with probes that are connected to a PC. The respirometer is submerged in a temperature bath, set at 31.0±0.5 ºC, and the pH is maintained at 7.5±0.5. The respirometer was inoculated with biomass from the municipal WWTP of Tarragona (Catalonia, Spain). The determination of Volatile Suspended Solids (VSS) was done according to the Standard Methods for the Examination of Water and Wastewater [87]. The values of VSS were 2100 + 320 mg $VSS \cdot l^{-1}$.

The biodegradability of the CWAO effluents was estimated by adding a substrate pulse of 8 mg COD l^{-1} (COD_{added}). Then, the Oxygen Uptake Rate (OUR) profile is obtained solving the oxygen balance in the liquid phase of the respirometer. The biodegradation parameter used to compare OUR profiles obtained in each experiment is the area under the OUR profile or oxygen consumption (OC). More information about the OUR calculation can be found elsewhere [68, 71].

VII.3. Results and Discussion

The results and discussion are divided into two sections. In the first one, the WAO and CWAO performance is discussed by means of Y_{COD} and Y_{TOC}. Also, the reaction mechanisms and intermediates are examined. Finally, in the last section, both processes are compared in terms of biodegradability enhancement.

During the discussion, the WAO and CWAO conditions will use the following nomenclature: 180-15 will refer to 180ºC and 15 bar of P_{O2}, 160-9 equals to 160ºC and 9 bar of P_{O2} and so on.

VII.3.1. DBS Disappearance: WAO compared to CWAO

Figure VII.41 shows the Y_{COD} and Y_{TOC} at 180ºC, 200ºC and 220ºC for different reaction times in WAO at 15 bar of P_{O2}. As expected, an increase in temperature gives a higher TOC abatement and COD removal (lower Y_{COD} and Y_{TOC}). For instance, a TOC reduction of 19, 34 and 47% were obtained at 180-15, 200-15 and 220-15 respectively. However, complete degradation of TOC and COD was not achieved, as the objective is to obtain an effluent with suitable intermediates to be biodegraded in a municipal WWTP.

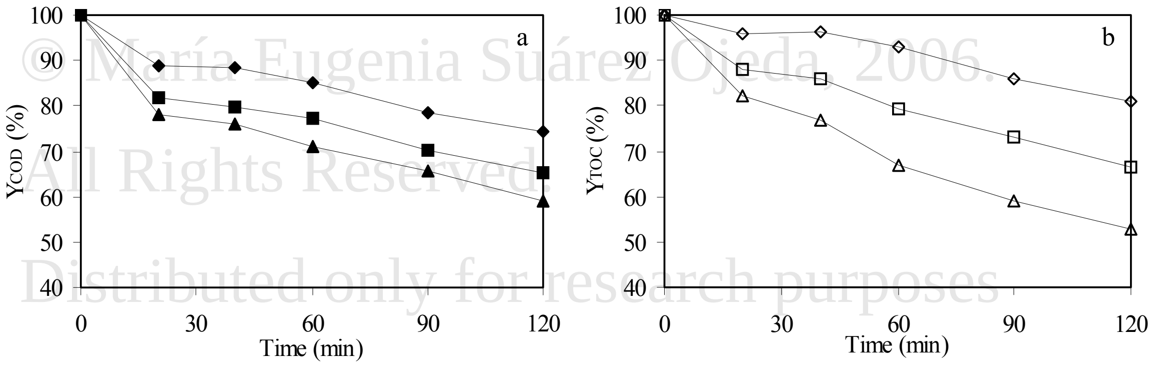

Figure VII.41. COD reduction (a-filled symbols) and TOC abatement (b-empty symbols) during WAO at 15 bar of P_{O2} of DBS at different temperatures. Symbols indicate experimental data {(♦ or ◊) 180ºC, (■ or □) 200ºC and (▲ or Δ) 220ºC}. Lines show trends.

For CWAO tests, Figure VII.42 shows the Y_{COD} and Y_{TOC} evolution in 72-h tests at 140ºC (empty symbols) and 160ºC (filled symbols). Figure VII.42a corresponds to the results at 2 bar of P_{O2}, whereas the results for 9 bar of P_{O2} are in Figure VII.42b. As previously found [113, 57], three different zones can be distinguished in all the cases. Firstly, after starting, an adsorption dominating period results in an apparent total COD and TOC removal. In a previous work [113], the DBS adsorption capacity of the AC used in the CWAO tests were established as 1028 ± 44 mg g AC $^{-1}$ (5 g l^{-1} of DBS), therefore, taking into account the liquid flow-rate and the feed concentration in the CWAO experimental set-up, the time needed to saturate the AC bed could be calculated, giving a value of 25 h, which roughly agrees with the time of apparent full conversion. Usually, a shorter time is observed in CWAO tests, which is probably related to the higher working temperature since adsorption capacity is well-known to decrease as temperature increases. This possibility is supported by the fact that the apparent total conversion period is even shorter at 160ºC. Once the AC bed approaches to steady state, a continuous and sudden rise in Y_{COD} and Y_{TOC} is observed. Finally, beyond 25 hours, once the bed is saturated with DBS, the Y_{COD} and Y_{TOC} almost attain a steady state. In the steady state period, which corresponds to the last 30 to 40 hours in each CWAO test, the steady state values of COD reduction are 25% at 140-2, 55% at 160-2, 16% at 140-9 and 14% at 160-9. Similar trends can be drawn for TOC removal. Actually, the behaviour regarding to temperature is typical at 2 bar, an increase in temperature leads to a remarkable increase in the COD and TOC removal, yet, in turn, it is not significant at 9 bar. However, it is surprising the fall in removals levels when the oxygen partial pressure increases at a given temperature. In addition, at 9 bar of P_{O2}, a high quantity of foam was observed in the sampling port and also in the reactor outlet. This non expected behaviour can be explained according to changes in the hydrodynamic operation as follows: At 9 bar of P_{O2}, the liquid flow pattern is laminar (Re=170) in the pipes before the reactor whereas the gas flow-pattern is turbulent (Re=6700). Consequently, when the aqueous DBS solution mixes with the turbulent air flow, a non-flowing foam phase is developed, causing a dramatic change in the operating regime of the reactor, which evidently harms its performance. At 2 bar of P_{O2}, both flow patterns are laminar (Re<2000) and no foam formation was observed.

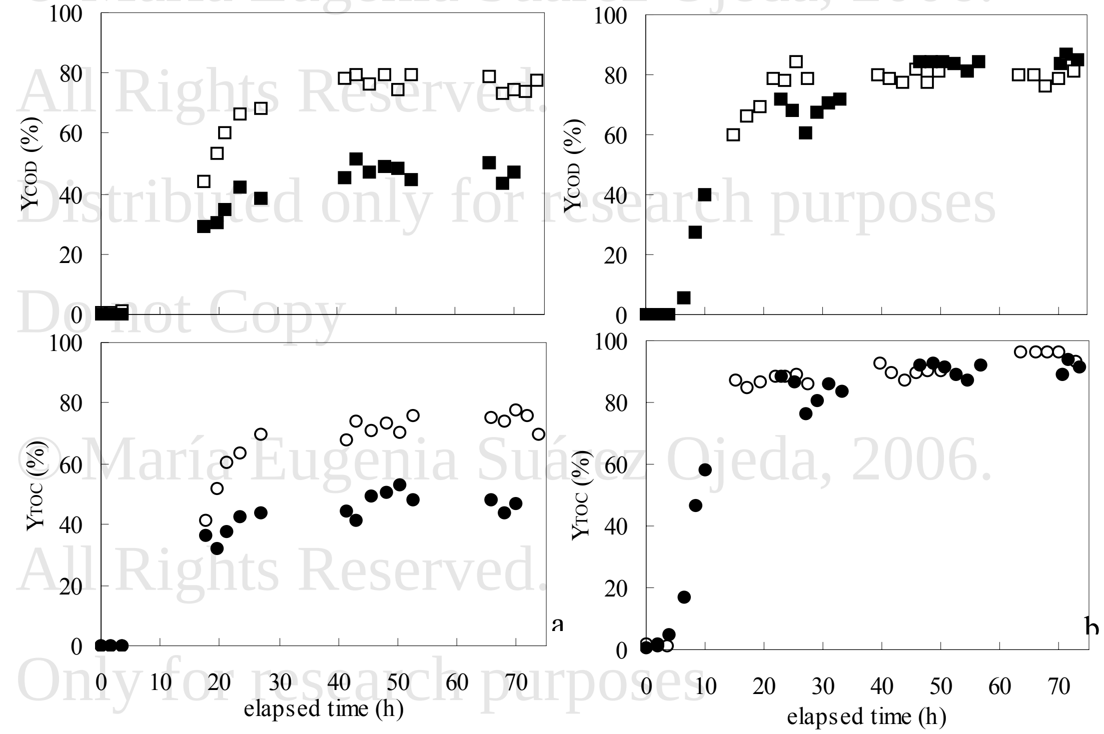

Figure VII.42. COD reduction and TOC abatement profiles during CWAO at 2 bar of P_{O2} (a) and at 9 bar of P_{O2} (b). Filled symbols correspond to 160ºC whereas empty symbols correspond to 140ºC. Symbols indicate experimental data; lines show trends.

Comparing both WAO and CWAO processes the use of AC as catalyst allows reducing the temperature and pressuring maintaining the removal of COD and TOC. For instance, in WAO at 220-15, the Y_{TOC} is 53% (Figure VII.41) whereas in CWAO at 160-2, the Y_{TOC} is 48% (Figure VII.42).

Regarding to reaction intermediates, the formation of organic acids as oxidation by-products in both processes was confirmed by HPLC analysis and pH of the effluent. The pH was left uncontrolled during all the experiments, but when DBS was subjected to WAO the pH decreased significantly up from 7.3 to 3.7, 3.6 and 3.3 after 120 min at 180-15, 200-15 and 220-15, respectively. In the case of CWAO experiments, the steady state pH was between 2.9 and 2.3. This decrease is caused by formation of organic acids as reaction intermediates as confirmed by HPLC analysis.

In WAO experiments, quantification of 4-sulfobenzoic acid and formic and acetic acids was done by means of HPLC using external standards. In order to calculate the contribution of each intermediate to the experimental COD, the theoretical oxygen demand (COD_{Th}) of each oxidation product was calculated using the empirical correlations obtained by Baker et al. [119] and the obtained HPLC concentration. The same procedure was applied to calculate the contribution of the intermediates to the experimental TOC.

Figure VII.43 shows the organic acids COD_{Th} (calculated from HPLC results) in the WAO effluent monitored during the reaction. A greater concentration of 4-sulfobenzoic acid was observed at higher temperatures. Especially during the initial oxidation step, concentration of 4-sulfobenzoic acid increases significantly, which is a consistent result as those of TOC and COD. Therefore, it can be expected that oxidation of initial DBS to short-chain sulfobenzene group via decarboxylation of alkyl side chain is the major route of WAO for DBS. Accumulation of acetic acid during oxidation increased with time and temperature. However, formic acid was variable and identified at very low concentration. Since formic acid is more reactive than acetic acid and oxidizes to carbon dioxide and water at temperatures as low as 150°C in WAO system, formic acid may react with other oxidation intermediates or undergo further oxidation.

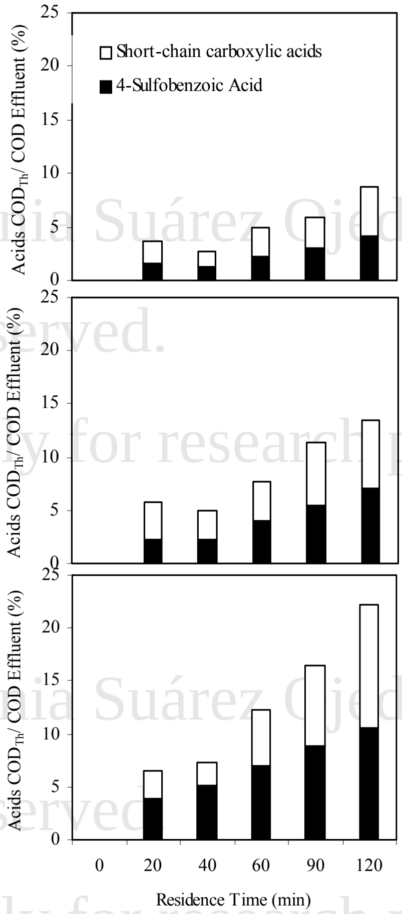

Figure VII.43. Acids COD_{Th} over COD in the effluent during WAO at 15 bar of P_{O2} of DBS at different temperatures: 180ºC (a), 200ºC (b) and 220ºC (c).

From the above results, 4-sulfobenzoic acid (representative of sulfo-aromatic group) and acetic acid (representative of short-chain carboxylic acids) could be regarded as major intermediates during WAO of DBS. Moreover, it is expected that there are three successive reaction steps for degradation of DBS in WAO system; decarboxylation of alkyl-side chain, aromatic ring cleavage including desulfonation and conversion of short-chain carboxylic acids to CO_2 and H_2O. Sulfo-aromatic groups such as 4-sulfobenzoic acid can be produced at the end of decarboxylation step, whereas short-chain carboxylic acids such as acetic acid may be generated during alkyl chain random scission and after aromatic ring cleavage. Furthermore, the content of 4-sulfobenzoic acid tended to increase with time under any given conditions. In HPLC analyses, other peaks appeared at low retention times, close to the peak corresponding to 4-sulfobenzoic acid and they also are likely to accumulate as intermediates. These unknown compounds are suspected to be refractory sulfonated aromatics such as sulfophenylcarboxylic acids [SPCs, $HSO_3C_6H_5(CH_2)_nCOOH$], sulfophenylaldehydes [SPAs, $HSO_3C_6H_5(CH_2)_nCHO$], sulfophenyldialdehydes [SPDAs, $(OHC)(CH_2)_mCH(CH_2)_n(CHO)C_6H_4SO_3^-$] and carboxylsulfophenylaldehydes [CSPAs, $(OHC)(CH_2)_mCH(CH_2)_n(COOH)C_6H_4SO_3^-$]. The above results suggest a consecutive-parallel reaction pathway, which agrees with the reaction pathway proposed previously by Patterson et al. [86].

In CWAO experiments, the reaction intermediates were also quantified by HPLC and the help of external standards. From Figure VII.44, the short-chain carboxylic acids fraction roughly increases with the increase of temperature in CWAO. Nevertheless, an increase in P_{O2} up to 9 bar, led to an unfavourable behaviour, lowering the short-chain carboxylic acids fraction, as can be seen in Figure VII.44 for 160-9 and 140-9 CWAO tests. As explained before, the drop in the reaction progress could be caused by the observed presence of a non-flowing foaming system which causes a poor reactor performance. Also, in this case, no 4-sulfobenzoic acid was detected but benzene sulfonic and 4-hydroxybenzene sulfonic acids were quantified in concentrations up to 25 and 100 mg l^{-1}, respectively

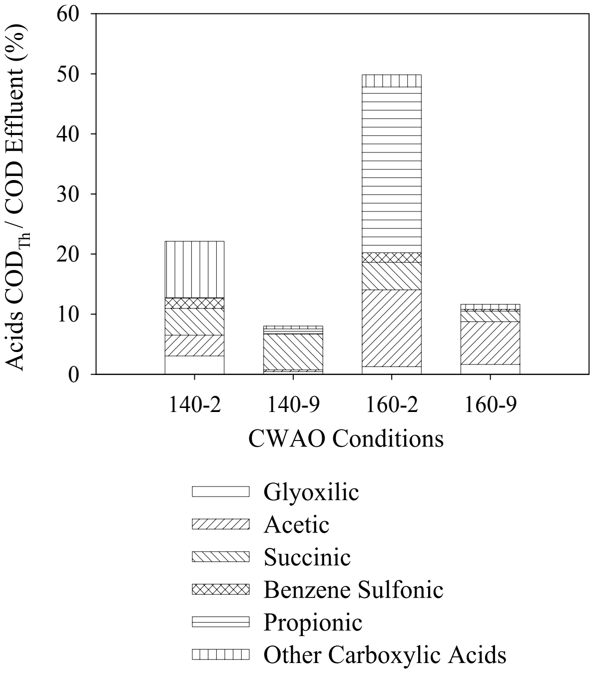

Figure VII.44. Acids COD_{Th} over COD in the effluent during CWAO at different conditions. Symbols indicate experimental data; lines show trends.

For instance, at 160-2 (which is the condition with the lowest Y_{COD} and Y_{TOC}) the majority of the remaining COD was in form of carboxylic acids (50%) and DBS (21%); the rest was in form of non-identified COD (27%), quinone-like products (1%) and condensation products (1%). Glyoxilic, formic, acetic, succinic, benzene sulfonic and propionic acids were 96% of the COD in form of carboxylic acids. In the case of 140-2, the effluent composition was mainly carboxylic acids (22%) and DBS (37%) whereas non-identified COD accounted for 39% and both quinone-like intermediates and condensation products were 1%.

Moreover, comparing Figure VII.43 and Figure VII.44, the fraction of carboxylic acids in the effluent from 140-2 and 160-2 is higher than in WAO experiments at 220-15, which confirms a deeper oxidation reaction.

From CWAO results, at 160-2 and 140-2 the reaction seems to evolve enough to oxidise most of the organic matter to glyoxilic, formic, acetic and propionic acids, which are the latest intermediates before total mineralisation. However, at 160-9 and 140-9, the acids are in lower proportion but also were of high molecular weight (results not shown) indicating that the reaction was not progressing enough. At those conditions the non-flowing foaming probably prevent the liquid flow from being in close contact with the AC, so the DBS oxidation does not progress deeply. In turn, it leaves the AC unprotected in front of undesired reactions such as surface oxidation and/or burning. The fact that activated carbon undergoes a high burning when is exposed to the same reacting conditions but in absence of any other organic compound was confirmed in a previous work [54].

To support the above speculation, the changes in the AC weight and in the AC textural properties during oxidation have been studied and should shed some light on the AC catalytic activity. Also, the influence of oxidative coupling reactions on CWAO could be assessed, because oxidation of DBS and its intermediates occur in parallel with AC oxidation/burning and coupling reactions. Table VII.26 shows the W_{AC} and the textural properties for the used AC from each CWAO experiment.

As Table VII.26 shows, W_{AC} was positive (i.e. the AC weight increased) by the end of the 140-2 and 140-9 tests. However, the W_{AC} was negative at the end of 160-9 and 160-2 tests. W_{AC} was also monitored [54, 57] for phenol CWAO in an identical experimental set-up and at identical conditions. W_{AC} turned out to be positive or negative depending on the time on stream and the operating conditions [54, 57]. Fortuny et al. [57] observed that the weight of AC used in phenol CWAO increased during the first 24 hours at 140-9, but, after that, it decreased to values below the original ones. However, after 10 days on stream, at 140ºC and at lower oxygen partial pressures than 2 bar, the AC weight always increased [57].

Table VII.26. Original bed loading, W_{AC} and textural characterization at the end of the CWAO tests.

Condition	140-2	160-2	140-9	160-9
Loaded AC (g)	7.01	7.03	7.00	7.00
WAC (%)^1	17.2	-46.7	6.0	-43.1
BET Surface Area (m2 g^{-1})	285	308	10	70
Micropore Volume (cm3 g^{-1})	0.006	0.014	0.001	0.002
BJH cumulative area surface (cm^2 g^{-1})*	148	185	8	49

* between 17 and 3000 Å

Several studies have shown that this positive W_{AC} can be attributed to the deposition of polymeric compounds produced by oxidative coupling reactions over the AC [103-105]. Cooney and Xi [90] demonstrated that, oxidative coupling reactions can be accelerated by the presence of a substituent in the phenol molecule at low pH. They postulated that oxidative coupling reactions occur simultaneously with the oxidation reaction and these coupling reactions probably block the active sites in AC, and decrease its catalytic activity.

Following this idea, a low W_{AC} gain i.e. small oxidative coupling, should correspond to a maximum in COD and TOC removal, since oxidative coupling is expected to block the active sites and to diminish the superficial area (as Table VII.26 shows) and, therefore, the catalytic activity. As can be seen in Table VII.26, all textural properties (BET surface, Micropore volume and BJH cumulative area surface) decrease following the order 160-2 > 140-2 > 160-9 > 140-9, although the highest impact is given by the operating pressure rather than by temperature. This order is actually the behaviour of COD and TOC removal and also matches the increasing concentration of carboxylic acids in the CWAO effluents.

According to the behaviour of the W_{AC} and the textural properties it could be estimated that oxidative coupling occurred in a greater extent than AC oxidation/burning at 140-2, whereas at 160-2, the AC oxidation/burning was higher than oxidative coupling reactions. At 140-9 and 160-9, oxidative coupling was higher or similar than AC oxidation/burning because AC was more directly exposed to the air as the lack pf DBS adsorbed left unprotected the AC surface.

TGA were performed to find out which kind of compounds could be responsible for the weight change and to evaluate the quantity of adsorbed products. Figure VII.45a and Figure VII.45b show the thermograms and their first derivatives (dw/dT) of the AC used in the CWAO of DBS and in the absorption isotherm described in chapter III.

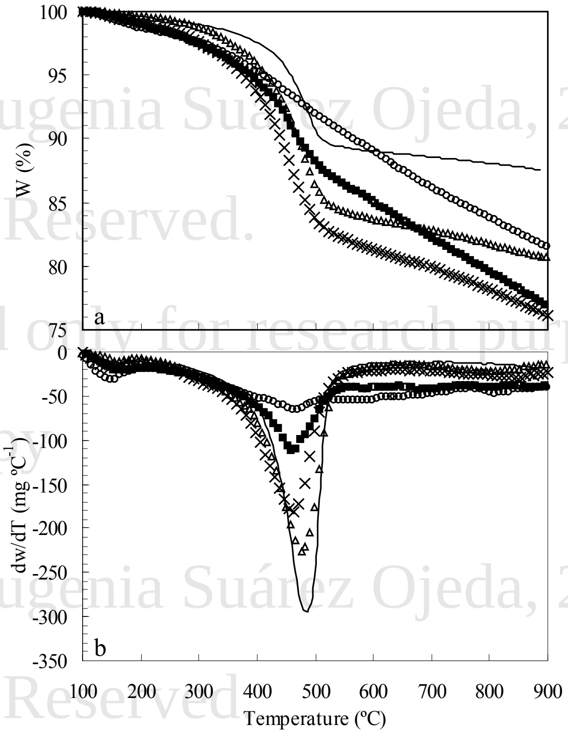

Figure VII.45. TGA data (a) and first derivative of TGA data (b) of used AC after being tested in 72 h CWAO experiments. {(×) 140-2, (Δ) 140-9, (■) 160-2, and (o) 160-9}. Continuous line corresponds to the TGA and derivative data of AC used to get the absorption isotherm [chapter III] of DBS.

Generally, as stated by Figuereido et al. [106], two zones can be distinguished in the thermograms from any AC. In the range 200-300ºC, the attached species, which are mainly, carboxylic groups, are slowly released as CO_2. Beyond that temperature, in the range of 300-900ºC, the evolving groups are CO_2 due to the decomposition of lactones and CO from oxygen surface groups such as carboxyl, phenyl and ethyl groups. However, three zones appears in the present thermograms of used AC and their derivatives (Figure VII.45a and Figure VII.45b). The weight loss in the first zone, peaking at 150ºC but extending up to 350ºC, roughly coincides with the release of physisorbed short-chain reaction intermediates. The weight loss in the second zone should correspond to the release of sulphur species coming from adsorbed DBS as confirmed by the thermogram and the derivative of AC used to obtain the adsorption isotherm of DBS. Finally, the third zone beyond 550ºC should match the decomposition of chemisorbed species, including the cracking of polymers from oxidative coupling reactions [107, 108].

The total weight loss (TWL) of each sample is summarised in Table VII.27 for all the used and the virgin AC. It should be noted that there is no significant difference between the TWL (from 18.6% to 24.1%) of each CWAO test. However, the samples coming from 160-2 and 140-2 tests have a higher TWL than the tests at 140-9 and 160-9 so, the quantity of irreversible adsorbed compounds (oxidative coupling) is higher in the first two cases than in the last two cases.

Table VII.27. Total weight loss (% w/w) during the TGA of the virgin and used AC

Virgin AC	DBS absorption	140-2	160-2	140-9	160-9
8.0	12.5	24.1	23.2	19.4	18.6

VII.3.2. Biodegradability enhancement

In this section, the dependence of the intermediates distribution and the AC behaviour on the operational conditions in the CWAO will be correlated with the measured biodegradability of each CWAO effluent. The objective is to find the best condition in the biodegradability enhancement which permits a successful coupling with an municipal biological WWTP.

The readily biodegradable COD fraction ($\%COD_{RB}$) of each CWAO effluent can be estimated using the heterotrophic yield coefficient (Y_H) calculated using the equations V.15 and V.16 stated in Chapter V.

Figure VII.46 shows the $\%COD_{RB}$ and a detailed distribution of intermediates for each CWAO effluent.

There was a lower OC at 140-9 and 160-9, probably because the concentrations of carboxylic acids have a minimum value and the high remaining DBS concentration could be inhibiting the biodegradation. The maximum $\%COD_{RB}$ (50%) occurred at a CWAO condition of 160-2. From Figure VII.46, the carboxylic acids had a maximum concentration at this condition. At 140-2, the $\%COD_{RB}$ (36%) was lower than the previous case being the carboxylic acids in lower proportion than at 160-2. In addition, the proportion of non-identified compounds, which was very high, should be considered. From HPLC chromatograms, at 140-9 and 160-9 the most of non-identified intermediates were in the retention times corresponding to quinone-like and aromatic compounds, probably being toxic or inhibitory intermediates [Chapter V]. On the contrary, at 160-2 and 140-2 most of the non-identified COD were in the retention times of carboxylic acids, which could be contributing to improve the effluent biodegradability. In fact, the values of COD_{RB} are always higher than the proportion of carboxylic acids, which could indicate that a non-identified intermediate or a non-detected co-metabolic effect was increasing the experimental OC in the respirometric tests [Chapter V]. However, it should be noted that, the biodegradability enhancement of DBS treated by CWAO is higher than the obtained when treating other phenolic compounds (Chapter V). For instance, for phenolic compounds, the better $\%COD_{RB}$ obtained were 36% for phenol at 160-2, 27% for o-cresol at 160-9 and 27% for 2-chlorophenol at 140-9, whereas in the case of DBS between 50 and 20%, which demonstrate that DBS undergoes higher oxidation than the other compounds.

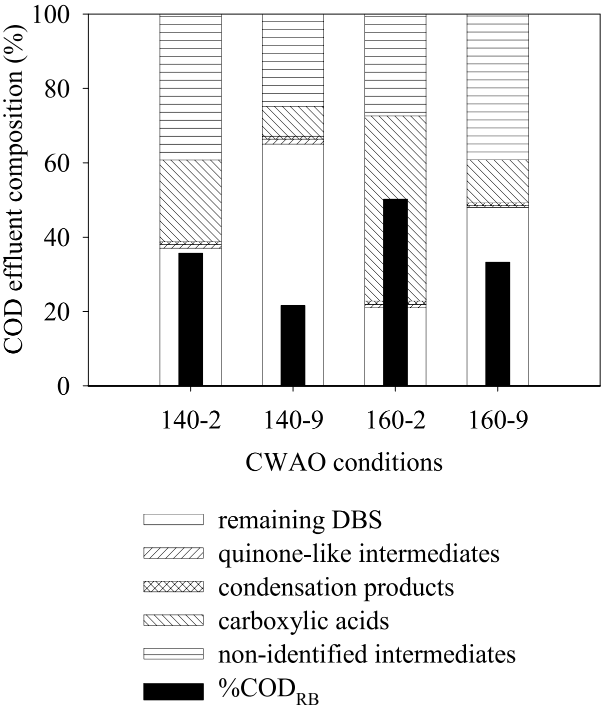

Figure VII.46. COD$_{Th}$ intermediates distribution (calculated from HPLC results) and biodegradability enhancement in CWAO effluents at the end of the tests.

As explained in Chapter V, three different factors should be considered when selecting the most suitable CWAO condition: the maximum COD conversion obtained in the CWAO, the maximum %COD$_{RB}$ and the catalyst preservation. In this case, the maximum COD conversion and the maximum COD$_{RB}$ were obtained at 160-2. Additionally, the AC conservation is clearly higher at 2 bar than at 9 bar. Based on these results, 160-2 should be an appropriated CWAO condition for DBS oxidation.

For WAO effluents no respirometry was made. Nevertheless, according to Chapter V acetic acid is a readily biodegradable intermediate from the CWAO of several substituted phenols. Therefore, the WAO biodegradability enhancement should be lower than in the case of CWAO since the readily biodegradable intermediates (just only acetic acid) in WAO effluents at 220-15 were in lower proportion (12% of the measured COD) than in CWAO experiments at 160-2 (50 % of the measured COD).

VII.4. Conclusions

DBS can be efficiently destroyed by both WAO and CWAO. The activated carbon without any active metal showed to have a catalytic effect on the CWAO of DBS, which allows lowering the temperature and pressure needed to maintain the same COD and TOC removals than in WAO. TOC reduction was between 19 and 47% for WAO experiments between 180 and 220ºC at 15 bar of P_{O2}, whereas for CWAO experiments at 2 bar of PO2 in the range of 140-160 ºC, the TOC removal was between 24 to 52%.

Concerning to the biodegradability enhancement of the DBS wastewater, CWAO increased the COD_{RB} up to 50% compared to the un-treated solution. The CWAO was highly selective to short-chain carboxylic acids when using 2 bar of P_{O2}. In turn, at 9 bar of P_{O2} the development of a non-flowing foaming system causes a poor reactor performance.

Factors influencing the CWAO performance such as adsorption, oxidative coupling reactions or pore blockage have been studied obtaining a fairly satisfactory explanation for the DBS reaction mechanism in presence of AC. The positive W_{AC} can be explained by the presence of attached polymers on the AC surface, which are probably produced by oxidative coupling reactions, as demonstrated by the results obtained with TGA and nitrogen adsorption isotherms.

VII.5. Acknowledgements

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CHAPTER VIII. GENERAL CONCLUSIONS AND FUTURE WORK

Outlook

The main objective of this research was to develop an effective combined chemical plus biological treatment for industrial wastewater containing refractory compounds. To follow this emerging concept, I proposed a technology that combines a first step of CWAO with activated carbon as catalyst, followed by a classical biological treatment with activated sludge.

The feasibility of this combined treatment was established through several steps. In the first part of this work, the feasibility of using AC as catalyst in the CWAO for other model compounds among phenol was demonstrated. Later, as second stage in this research, the optimal severity of CWAO step was established, taking into account the target pollutant removal, AC catalyst preservation, distribution of partial oxidation products and biodegradability enhancement. The biodegradability of CWAO effluents was found by respirometry and a detailed analysis of the toxicity or inhibitory effects of each one of the main intermediates detected into the oxidation route was performed. Finally, with these data, an activated sludge plant at pilot scale was designed and a coupling strategy and an acclimatisation procedure for the inoculated microorganisms were developed by increasing the organic load of CWAO effluents in the influent to the pilot plant.

VIII. 1 General Conclusions

The most relevant conclusions of this work are:

- The feasibility study of CWAO performed at 140-2 showed that the AC without any supported active metal behaves bifunctionally as adsorbent and catalyst, and was active enough to oxidise phenol, o-cresol, 2-chlorophenol and DBS. On the contrary, aniline, sulfolane, p-nitrophenol and nitrobenzene were still refractory to the CWAO at these conditions. Therefore, phenol, o-cresol, 2-chlorophenol and DBS were kept as the target compounds for the rest of the work.
- Target pollutant disappearance, COD removal, TOC abatement, distribution of partial oxidation products and biodegradability enhancement were very sensitive to temperature but almost independent of the oxygen partial pressure (P_{O2}). On the contrary, AC catalyst preservation was strongly influenced by both temperature and P_{O2}.
- The reactivity of the target compounds was different depending on the operating conditions and catalyst behaviour. Two different reaction mechanisms, electrophilic or nucleophilic substitution, can explain the conversion achieved depending on the operating conditions. However, conversion is also affected by kinetics and catalyst performance and the prevalent mechanism cannot be sufficiently assessed. As both mechanisms are based in the presence of oxygen species, the AC could be envisaged as a promoter in the generation of oxygen radicals and anions, which respectively behaves as nucleophiles and electrophiles in the reaction media.
- Using respirometric tests, the CWAO main intermediates were classified as readily biodegradable, inert or toxic/inhibitory. Among the carboxylic acids, the readily biodegradable intermediates were fumaric, propionic, acetic, succinic, formic and glyoxylic acids, whereas oxalic, maleic, malonic, 4-HB and salicylic acids were classified as inert intermediates. Quinone-like products behaved as inert intermediates at 1 mg COD l^{-1}, but they became inhibitory (catechol) or toxic (hydroquinone and *p*-benzoquinone) intermediates at 4 mg COD l^{-1}. The target pollutants were classified as inert intermediates, however o-cresol became inhibitory at high concentrations.
- The respirometric procedure is a useful screening method to determine the effect of each CWAO intermediate over an activated sludge and it can help to decide the best way for coupling both treatments.

- The best CWAO condition for the pre-treatment phenol, o-cresol and 2-chlorophenol was 160-2. At this condition, the X_{COD} was the highest one for phenol and 2-chlorophenol and just the second one for o-cresol. In addition, the catalyst preservation was clearly better at 2 bar at 9 bar of P_{O2}. Finally, the $\%COD_{RB}$ was the highest for phenol and almost the maximum for o-cresol and 2-chlorophenol.
- The biodegradability of a CWAO effluent could be predicted knowing its composition, the concentration and the biodegradation properties of the main intermediates.
- Tested for phenol and o-cresol, the integrated CWAO-biological treatment achieved more than 90% of COD removal without any undesirable effect on the biomass using a proportion of 30% of CWAO effluents in the inlet of the municipal pilot scale WWTP Therefore the CWAO coupled with a biological municipal WWTP is a feasible treatment for wastewater containing o-cresol in terms of efficiency, operation and legislation.
- For o-cresol and phenol removal by means of WAO, the readily biodegradable intermediates were in lower proportion and the possible toxic/inhibitory intermediates were in higher concentration than in CWAO, which renders a better biodegradability enhancement of the CWAO treatment.
- For 2-chlorophenol, both WAO and CWAO were suitable technologies, in terms of biodegradability enhancement and therefore the final selection of the treatment should be based on technical and economic feasibility or availability.
- DBS can be efficiently destroyed by both WAO and CWAO. However at 9 bar of P_{O2} the development of a non-flowing foaming system causes a poor reactor performance in the CWAO system. The biodegradability enhancement of DBS treated by CWAO is higher than the obtained when treating other phenolic compounds.

VIII. 2 Future Work

Clearly, the efficiency of a coupled chemical plus biological oxidation process depends, in general, on the target pollutant and/or the composition in the case of a real industrial effluent. It would be, thus, very interesting to perform comprehensive comparative studies involving several oxidation techniques both chemical and biological. Further research should be focussed on finding optimal conditions for the respective treatment depending on the refractoriness of the target pollutants.

For instance, a more deep study of the AC behaviour should be addressed. Optimal behaviour of AC depends on the structure type (granular, nanostructure), the surface area, the pore volume distribution and the kind of surface chemistry, which are determined by the experimental conditions used during the preparation or production step. There is a lack of systematic comparison between different ACs, which is an essential step for an extensive use of this kind of materials in environmental applications and catalysis.

Also, the conventional municipal WWTP are not capable of dealing with industrial wastewater, therefore the only option for these plants is to retrofit and optimise the existing process. The optimisation of biological treatments is a challenge and the use of bioaugmentation, biofilms instead conventional activated sludge, and different system configurations should be addressed.

Finally, a detailed kinetic and reactor modelling are required to assess the potential of the oxidation techniques for its successful application and scale-up. Such studies may also improve the precision of economical balances that are important criteria for the industrial application in any process.

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ANNEX I

PICTURES OF ALL THE EQUIPMENTS USED DURING THIS WORK

The printed version contains a CD with pictures of all the equipments used during this work

ANNEX II

PRELIMINARY RESULTS FROM RESPIROMETRIC TESTS OF CARBOXYLIC ACIDS

COD_{Added}	5 mg COD l^{-1}								
Acids	oxalic	formic	malonic	**acetic**	maleic	succinic	fumaric	acrylic	4-HB
OUR_{MAX} (mg COD mg SSV^{-1} d^{-1})	0.1	0.1	0.0	**0.2**	0.0	0.1	0.4	0.0	0.0
OC (mg COD l^{-1})	0.6	2.1	0.0	**1.3**	0.0	1.6	1.0	0.0	0.0

Not readily biodegradable if OC equals to zero.
Readily biodegradable if OC and OUR_{MAX} are higher or equal than those obtained with acetic acid.