Graduate Studies in Chemical and Process Engineering

Tailoring activated carbons as catalyst for catalytic wet air oxidation of phenol

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El Dr. Josep Font, Profesor Titular del Departament d'Enginyeria Química de la Universitat Rovira i Virgili de Tarragona,

Fa constar que el present treball, amb el títol

Tailoring activated carbons as catalyst for catalytic wet air oxidation of phenol

que presenta la doctoranda na Maretva Baricot Mendoza per optar al grau de Doctora per la Universitat Rovira i Virgili, ha estat dut a terme sota la meva immediata direcció i que tots el resultats obtinguts són fruit del projecte de recerca realizat per l'esmentada doctoranda al programa de doctorat Graduate Studies in Chemical and Process Engineering de dita universitat.

I per a què tingui els efectes que corresponguin, signo aquesta certificació.

A Tarragona, 2 de maig de 2008

The goal of life is living in agreement with nature.
Zeno (335 BC - 264 BC)

Never discourage anyone...who continually makes progress, no matter how slow.
Plato (427 BC - 347 BC)

I am among those who think that science has great beauty. A scientist in his laboratory
is not only a technician: he is also a child placed before natural phenomena which
impress him like a fairy tale.
Marie Curie (1867 - 1934)

A mis padres, Egleé y Manuel,
Porque me enseñaron a ser valiente y la importancia de no darme por vencida,
y porque velan por mí cada día a pesar del océano que nos separa.

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SUMMARY

Since the development of industrial activities in the whole world and specially nowadays, the access to clean water is more and more difficult. Over the past century our water consumption increased tenfold and, according to the World Health Organization, 1.1 thousand million people have no access to clean drinking water, while 2.4 thousand million lack proper sanitary provision. In addition, only 0.8 % of the world stock of water is actually fresh water, so that serious considerations on the availability of a constant supply of fresh water should be done. With this in mind, the need to have different techniques available to treat wastewater arises as a main concern, considering the great variety of chemical industries and activities than can produce contaminated effluents. Therefore, the detoxification of polluted water and its recycling when possible is mandatory for a sustainable and sustained development.

For wastewater containing low to medium pollutant load, Catalytic Wet Air Oxidation (CWAO) yielded satisfactory results in laboratory studies, with the advantage that relatively mild operating conditions are needed, leading to lower investment and operation costs. Besides, the use of low cost effective catalysts can largely improve the overall performance of the treatments. Some activated carbons (AC) have been successfully used as catalyst in the CWAO of phenol in a trickle bed reactor (TBR) configuration. However, the reason for the catalytic activity of AC in CWAO is not yet completely understood. Some partial studies on the catalytic behaviour of effective activated carbons, which were subjected to modifications, showed a decrease (few times an increase) in its capacity for oxidising phenol. This suggests that modifications of the AC properties can have a large impact in its performance.

The objective of this work is to identify properties potentially responsible for the catalytic activity shown by some carbonaceous materials. With this goal, eight commercial activated carbons were tested as received and modified by several means (thermal treatment, acid wash and metal impregnation) and its catalytic performance evaluated in the oxidation of phenol. These modifications intended to highlight the effect of the surface oxygen functionalities, textural properties, i.e. surface area and pore volume, and iron (and other metals) content. Simultaneously, the activated carbons were physically and chemically characterised.

The results demonstrate that thermal treatment is effective for elimination of surface oxygen functionalities from carbon. The removal of surface oxygen enhances phenol adsorption, thus all thermally treated samples showed an increase in the adsorption capacity. However, the decrease in the surface acidity due to the removal of acidic oxygen groups did not modify the catalytic behaviour of samples.

Neither the increase of the mesoporosity modified the catalytic performance. Actually, the characterisation of the used activated carbons demonstrates that over 80% of the initial surface area and original micropore volume were lost after being on stream, but the carbons still showed catalytic activity. This indicates that textural properties did not have influence in the catalytic behaviour of carbons. Instead, it was evidenced that other parameters may have greater influence in the catalytic activity of this material, since three carbons made from vegetable raw materials, specifically wood and coconut shells

did not show any catalytic behaviour at all. This indicates that raw material, specially the mineral matter that could be present in the final activated carbon, could be contributing to the catalytic behaviour, since mineral matter is mainly formed by metals and its oxides. Actually, all the commercial carbons showing catalytic properties are made from coal and they have noticeable amounts of iron, being a clear correlation between the presence of iron and their ability for oxidising phenol. This fact was demonstrated by demineralising the activated carbon and then conducting impregnation on iron. Demineralised activated carbons gave lowered phenol conversions. In turn, iron impregnated activated carbons showed remarkable catalytic activity, even higher than that shown by the commercial parent activated carbons. Even, a different commercial AC, which originally showed no activity for phenol oxidation, was capable of achieving a substantial improvement, giving 30% of phenol conversion, after iron impregnation.

These results confirm the hypothesis that mineral matter, specifically iron, is mainly responsible for the catalytic behaviour of activated carbons in the CWAO of phenol. However, having iron is not enough to be catalytically active in this reaction. It is necessary iron to be actually available in the carbonaceous matrix and in an appropriate state. Some final attempts for preparing tailored activated carbon from different raw sources still failed due to the lack of iron availability in the carbon matrix or the low mechanical stability of the material.

The findings described in this PhD thesis open the doors for a better designing of tailored activated carbons from costless raw materials, allowing cheaper catalytic activated carbons to be available for wet oxidation of phenol. This fact should contribute to the wider implementation of CWAO for recovering polluted aqueous effluents that are reluctant to biotreatment.

PhD Student: Maretva Baricot Mendoza
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RESUMEN

Debido al marcado desarrollo que han tenido las actividades industriales en el mundo, el acceso al agua potable es cada vez más difícil. Durante el último siglo el consumo mundial de agua se ha incrementado 10 veces y de acuerdo con información de la Organización Mundial de la Salud 1.1 miles de millones de personas no tienen acceso a agua potable y 2.4 miles de millones no disponen de las condiciones sanitarias apropiadas. Adicionalmente, sólo 0.8% de la reserva global de agua es apta para el consumo humano, por lo que serias medidas deben ser tomadas para garantizar un suministro constante de agua a la humanidad. Surge entonces como una necesidad, disponer de diferentes tecnologías de tratamientos de aguas residuales, especialmente considerando la gran variedad de industrias químicas existentes hoy en día, cuyos desechos son, en la mayoría de los casos, no sólo contaminantes sino también tóxicos para los seres vivos. Finalmente, es necesaria la purificación de los efluentes industriales para su posible reutilización si se pretende garantizar el desarrollo sustentable de la sociedad.

La oxidación húmeda catalítica con aire (CWAO) es un tratamiento que ha demostrado ser eficiente para el tratamiento de aguas residuales con cargas orgánicas bajas o medias, al menos experimentalmente. Esta técnica posee la ventaja de ser eficiente incluso operando en condiciones moderadas de temperaturas y presión, lo que se refleja en bajos costos de instalación y mantenimiento. Si adicionalmente, el catalizador utilizado es de bajo coste, este tipo de tratamiento podría promoverse más fácilmente. Algunos carbones activos comerciales han sido empleados exitosamente como catalizadores en la CWAO de fenol en un reactor de lecho fijo de goteo. Sin embargo, las razones por las que este material presenta actividad catalítica no han sido completamente esclarecidas. Algunos estudios preliminares han demostrado que al realizar modificaciones en las propiedades de los carbones que presentan capacidad catalítica, generalmente se produce también una disminución en su capacidad para oxidar fenol.

Por esto, el objetivo de este trabajo de investigación es identificar las propiedades potencialmente responsables de la actividad catalítica del carbón activo. Para ello, se utilizaron ocho carbones activos. Los mismos fueron modificados mediante tratamientos térmicos, lavados con ácidos y por impregnación de metales. Los carbones originales y de todas las muestras resultantes de las modificaciones fueron utilizados como catalizadores en la CWAO del fenol, con el objetivo de evaluar el impacto de parámetros como las propiedades físicas (área superficial y porosidad), el contenido de grupos funcionales oxigenados y el contenido de hierro y otros metales en la actividad catalítica.

Las conclusiones más importantes de este trabajo se enuncian a continuación:

1. El tratamiento térmico en atmósfera inerte resultó efectivo para eliminar los grupos superficiales que contienen oxígeno de la superficie del carbón y que se forman generalmente durante la etapa de activación. Al ser la temperatura máxima del tratamiento 900ºC, luego de éste quedan aún sobre el carbón algunos grupos de carácter básico, como carbonilos. El tratamiento en hidrógeno fue efectivo no sólo para remover los grupos funcionales oxigenados de la superficie del carbón, sino también para estabilizarla al reaccionar con los sitios activos formados por la descomposición de estos grupos funcionales.
2. La eliminación de los grupos funcionales de carácter ácido incrementó la capacidad de adsorción de fenol, ya que promueve los mecanismos propuestos como responsables de la adsorción de fenol sobre el carbón activo. Por un lado favorece la formación de los complejos donador-aceptor de electrones entre el anillo aromático del fenol como receptor y los grupos carbonilos que quedan en la superficie del carbón como donadores. Por otro lado, hay un aumento en las interacciones π-π entre los electrones π del plano basal del carbón y el anillo aromático del fenol.
3. Igualmente, la reducción de la acidez de la superficie por la eliminación de los grupos funcionales, reduce también su carácter hidrofílico, evitando la formación de grupos de moléculas de agua que luego bloquean los sitios activos para la adsorción de fenol. Esta reducción de la acidez se evidenció en los altos valores de pH_{pzc} mostrados por todos los carbones tratados térmicamente, con nitrógeno o hidrógeno.
4. El tratamiento térmico no modificó las propiedades físicas de los carbones, ni el área superficial ni el volumen de poros. Esto significa que la capacidad del adsorción de fenol del carbón activo puede ser mejorada mediante un tratamiento térmico que en realidad no modifica su porosidad.
5. Sin embargo, ni la mejora en la capacidad de adsorción ni la reducción de los grupos superficiales produjeron mejorías en la actividad catalítica mostrada por los carbones originalmente. Esto demuestra que las propiedades químicas de la superficie del carbón activo ni la capacidad de adsorción son factores claves en la capacidad catalítica del carbón activo en la oxidación del fenol.
6. El volumen de mesoporos no parece haber contribuido decisivamente con la actividad catalítica mostrada por los carbones activos. Las muestras preparadas a partir del carbón HD, las cuales son altamente mesoporosas, mostraron una actividad catalítica pobre. Sólo se observó un ligero incremento en la conversión obtenida con HDDSH, más bien atribuida a la formación de compuestos poliméricos de fenol adheridos a la superficie, los cuales pueden ser generados por la meso y microporosidad incrementada de la muestra, permitiendo una mayor adsorción de fenol durante las primeras horas de operación en el reactor. Sin embargo, la muestra MESCa, que también tiene un mayor volumen de mesoporos que el carbón original ME, no mostró ninguna mejora en su capacidad para oxidar fenol, debido a que la conversión obtenida con estos dos carbones es prácticamente idéntica, 42% y 45%, respectivamente.
7. La desmineralización de la muestra ME provoca una reducción importante en la conversión de la oxidación de fenol, disminuyendo de 45% a 25%. Este resultado demuestra que la materia mineral, específicamente hierro que es el metal

encontrado en mayor cantidad en este carbón, tiene una gran influencia en la actividad catalítica de este material. Esto se confirma con el hecho que, tres carbones activos comerciales con altos valores de área superficial y un alto volumen de microporos, pero con ningún tipo de material mineral presente debido a la naturaleza del material con que fueron fabricados, no muestran un comportamiento catalítico en la oxidación del fenol.

8. El contenido de hierro del carbón activo ha mostrado estar estrechamente relacionado con la actividad catalítica mostrada en la CWAO del fenol en un TBR. Incrementando 3.5 veces la cantidad de hierro en el carbón original ME, es posible aumentar la conversión fenol hasta un valor del 80%, como es observado con las muestras MENFe y MESCaFe.

9. La ubicación del hierro en la matriz del carbón activo parece ser crítica para el comportamiento catalítico subsecuente en la oxidación de fenol. Análisis realizados con varios carbones activos comerciales demostraron que, aún teniendo el mismo contenido de hiero, dos carbones como ME y CN exhiben diferentes comportamientos catalíticos, arrojando dos conversiones diferentes (45% y 30%). Por otro lado, ambos carbones mostraron selectividades diferentes en la distribución de los productos intermedios de la oxidación de fenol. Esto parece indicar que no sólo el contenido de hierro es necesario para mostrar un comportamiento catalítico, sino que también es necesario que el hierro esté realmente apto para actuar como catalizador.

10. La activación en una sola etapa resultó ser efectiva para elaborar carbones activos a partir de conchas de coco, obteniendo carbones con altos valores de área superficial y de volumen de microporos. A pesar de que el carbón MCS posee un área superficial 34% menor que el carbón comercial ME, ambos muestran la misma capacidad para adsorber fenol. Sin embargo, y debido a la ausencia de material mineral en este carbón, MCS no demostró ningún tipo de actividad catalítica para la oxidación del fenol. El carbón MCSFe, que también fue hecho a partir de coco, pero incluyendo una etapa de impregnación de hierro antes de la activación, tampoco mostró comportamiento catalítico en esta reacción. Esto indica que, a pesar de tener un contenido de hierro similar al de F400 o IR, dos carbones activos hechos a partir de carbón mineral, este hierro no es catalíticamente activo. En conclusión, el hierro en los materiales carbonosos no siempre muestra actividad catalítica, debido bien sea a su ubicación en el carbón o a la fase cristalina en que se encuentra.

11. La impregnación de hierro es más efectiva cuando se realiza en materiales carbonosos previamente tratados con ácido, para formar grupos acídicos en la superficie. Estos grupos ácidicos debido a sus propiedades para el intercambio iónico, mejoran la adsorción de hierro que luego será fijado a la matriz carbonosa con un tratamiento térmico en nitrógeno.

12. Es posible, mediante la incorporación de hierro, dotar de actividad catalítica a un carbón activo comercial, que inicialmente no mostraba capacidad catalítica en la oxidación húmeda del fenol. El contenido de hierro del carbón GT, fabricado a partir de conchas de coco, fue aumentado hasta un 0.3% wt. Finalmente, con este carbón, que poseía hierro impregnado, el GTNFe, se obtuvo una conversión del 30% en estado estacionario.

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Chapter I

> "Access to safe water is a fundamental human need and therefore, a basic human right. Contaminated water jeopardizes both the physical and social health of all people. It is an affront to human dignity."
> ***Kofi Annan, United Nations Secretary-General. Message on World Water Day 2001***

Introduction

1.1. Fresh Water World Supply. Facts.

1.1.1. Water Supply and Sanitation

Water has always been a key factor for the development of humankind. Since humans started to establish permanent settlements and adopted an agrarian way of life (about 10000 years ago), these societies became highly dependent on water. Ancient great civilizations were actually built around water sources like rivers. In fact, from written sources and archaeological excavations it is now known that Greeks and Romans were aware of the importance of water for the health of people. Signs have been found that they used to apply settling tanks, sieves, filters and even boil water as methods to improve the quality of the water. However, with the start of industrialisation and the growth of cities, not only the supply of water became an important issue, also it was necessary to develop sanitation systems to ensure public health. With the extensive growth of population during the 20th Century (global population quadrupled, urban population increased thirteen times, industrial production forty times and energy consumption ten times) the number and complexity of biological and chemical hazards in water has considerably increased, too (Vuorinen et al. 2007).

Surprisingly, (or maybe not) some things have not changed since 2000 years ago. In Romans age "*The rich had* running *water in their homes; the poor had to fetch their water from public fountains. The rich had their own baths and toilets, the poor had to use public toilets and baths. All this must have caused differences in the health of rich and poor people*" (Vuorinen et al. 2007). That fact has not changed in more than 2000 years of human development.

In any report from World Health Organisation (WHO) or United Nations (UN) dealing with water, sanitation and health, the following facts can be read[1]:

- ✓ Currently, around two milliard people lack access to truly potable water.
- ✓ Nearly 2 million children die each year from waterborne diseases, which is more than 5000 daily.
- ✓ It is estimated that 60 million children per year suffer from stunted growth and development due to waterborne diarrhoeal diseases.

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[1] Water, sanitation and hygiene links to health, World Health Organization.http://www.who.int/water_sanitation_health/publications/facts2004/en/index.html.

- ✓ At any given time, patients suffering from waterborne diseases occupy 50% of the world's hospital beds. In some developing countries, the figure reaches 80%.
- ✓ Women in developing countries spend an average of six hours every day collecting water. This time could be used in learning or working, which could represent an improvement in the economy of the family.
- ✓ Debilitating, even deadly diseases result from drinking and using unsafe, non-potable water. Diseases like cholera, diarrhoea, hepatitis and malaria are among them.
- ✓ Around 2 million people are killed yearly by diarrhoeal diseases and malaria, being 90% children under age of 5.

It is understandably why water was asserted as a Human Right by the UN in 2002, at their General Comment No.15: "The human right to water entitles everyone to sufficient, safe, acceptable, physically accessible and affordable water for personal and domestic use". This clarified the obligation for governments to extend access to sufficient, affordable, accessible and safe water supplies and to safe sanitation services as their resources allow.

However, according to the Human Development Report 2006 of the UN, the bottom problem is not actually water scarcity. It stated that "*the roots of the crisis in water can be traced to poverty, inequality, and unequal power relationships, as well as flawed water management policies that exacerbate scarcity*" (Human Development Report 2006). An uneven distribution of water on earth is the cause that, for example, Latin America has twelve times more water per person than South Asia, or than a country like Yemen has 198 m^3 per person available whereas Canada has an average of 90000 m^3 per person. In United States for instance, the daily consume of water per inhabitant is about 575 litres, but in Mozambique this figure decreases to 4 litres per day, far from the Water Poverty Threshold value, which is 50 litres per day. Although establishing an accurate value for the desirable consumption of water per person could be complicated, because other factors are involved, e.g. local availability and water infrastructure, it cannot be denied that measures should be taken in order to make water, at least more available in some areas of the world.

1.1.2. Water uses

According to the Food and Agriculture Organization of UN, agriculture is the first user of water worldwide, accounting for about 70% of all freshwater withdrawn from lakes, rivers and aquifers.

A non proportional increase in the use of water for agricultural activities can be explained by the fact that, during the last 50 years, not only the world population has grown considerably. Also, as world get wealthier, they eat more, so that not only their consumption of water *per se* increases, but also the amount of water needed to produce the food they will eat (it takes 3500 litres to produce the food to cover the minimum of 3000 kcal). Even the food habits have impact on water consumption. Growing one kilo of rice takes 2000 to 5000 litres of water, or it takes eight times more water to grow a tonne of sugar than a tonne of wheat, for instance. Higher values can be seen when talking about meat: it is necessary 13000 to 15000 litres of water to produce one kilo of grain-fed beef (Human Development Report 2006).

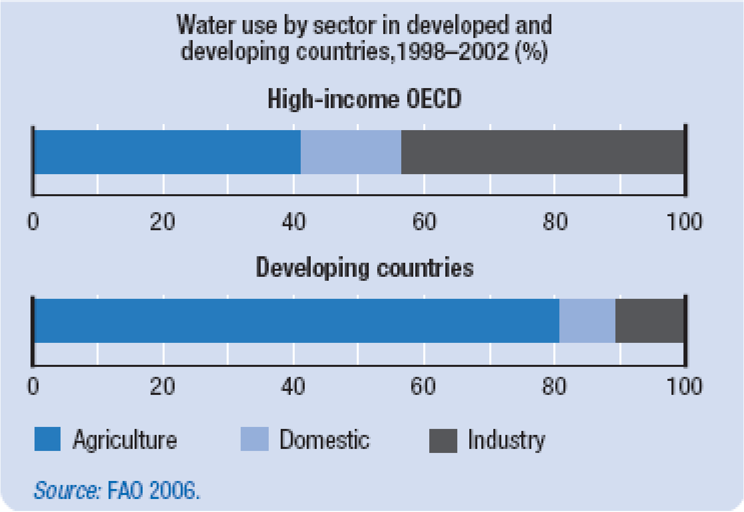

Figure 1.1.1. How the world use its water (Human Development Report 2006).

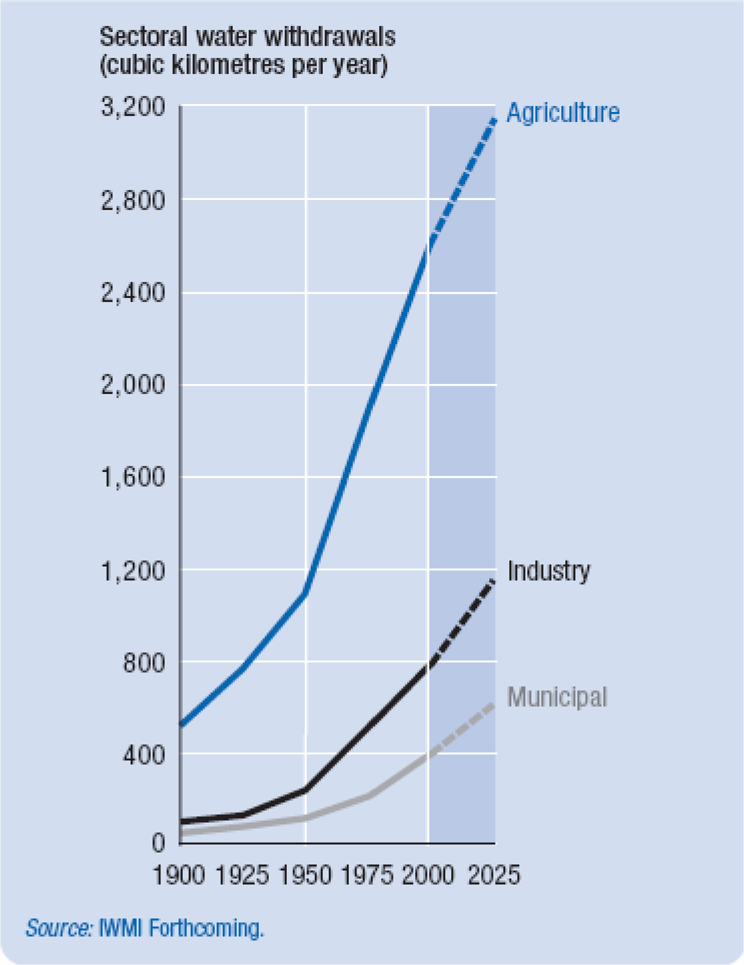

Figure 1.1.2. Water use by sector (Human Development Report 2006).

1.1.3. Groundwater and Water Scarcity problem

Groundwater is the water contained beneath the surface in rocks and soil, and is the water that accumulates underground in aquifers. Groundwater constitutes 97% of global freshwater and is an important source of drinking-water in many regions of the world. In many places, groundwater sources are the single most important supply of drinking-water, particularly in areas with limited or polluted surface water sources[2].

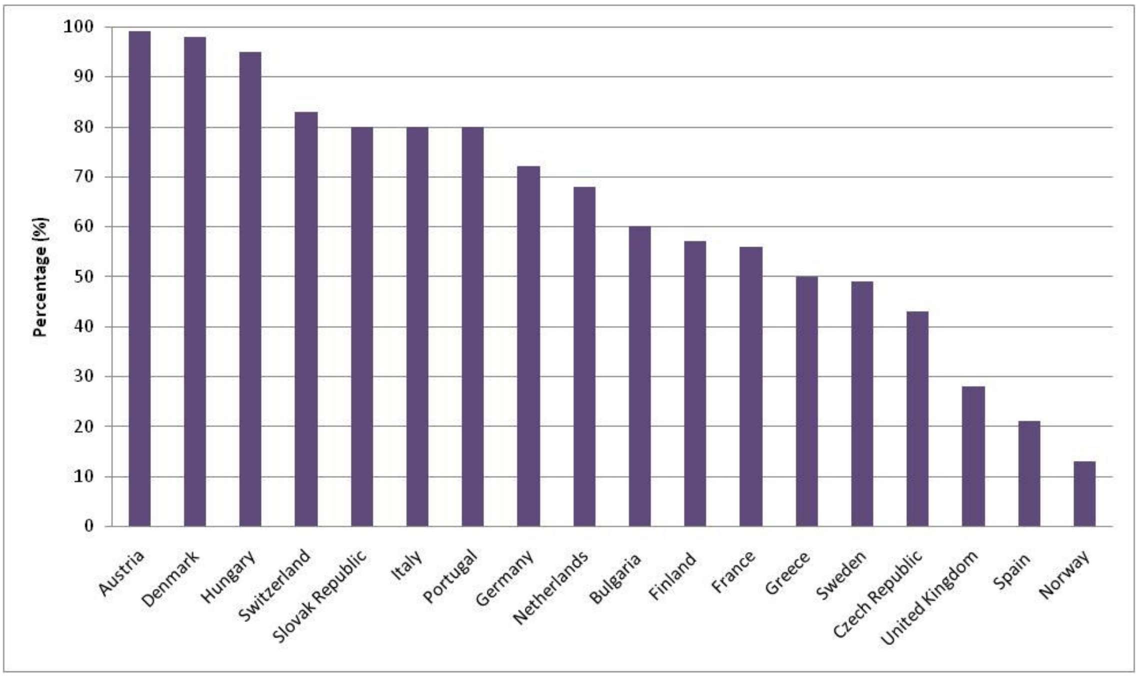

Figure 1.1.3. Proportion of groundwater in drinking-water of European countries.[2]

Figure 1.3 shows that reliance upon groundwater varies considerably between countries. Spain, for example, takes only 20% of its drinking water from groundwater sources, whereas Austria and Denmark use groundwater resources as unique supply for drinking water.

However, groundwater represents just 0.62% of the water on Earth. In fact, fresh and unfrozen water constitute only 0.65% of the water in the planet. A distribution of the total renewable fresh water resources per capita in the World is represented in Figure 1.1.4. Fortunately, the global climate change experienced during the last decades has emphasised the world water concern. The increase in global temperatures potentially causes rising sea levels, changing patterns of precipitation, floods and droughts, changes in biota and food productivity and increase of infectious diseases. These effects will have major impact on socio-economic sectors, such as agriculture, and on water resources (Environmental Signals 2002). Specifically 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 the Mediterranean (The European Environment:

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[2] Protecting groundwater for health: managing the quality of drinking-water sources (Work in progress and drafts), October 2004, WHO.

State and outlook, 2005). For all these reasons, a responsible use of water in all activities (domestic and industrial) is necessary.

According to data from UN Development Program Report 2002, the average water use per person per day in Spain was around 320 litres (in Germany this value was 193 litres, almost the half of the consumption in Spain). The Spanish National Statistics Institute reported that by year 2004 the amount of water consumption per person per day was of 381 litres (48% more than in 1996). Surprisingly, the wastewater produced in Spain the same year was 377 litres per person per day. This means, that if the total amount of wastewater produced in Spain could be treated to make it reusable, it would cover 99% of the daily water needs per person in the country. This situation is probably similar in several countries and it strengths the fact that reuse of available water is a key factor to afford a sustainable society. However, the increasing complexity of chemical compounds used in nowadays industry, which are later poured in environment, represents a challenge for the wastewater treatment technology field.

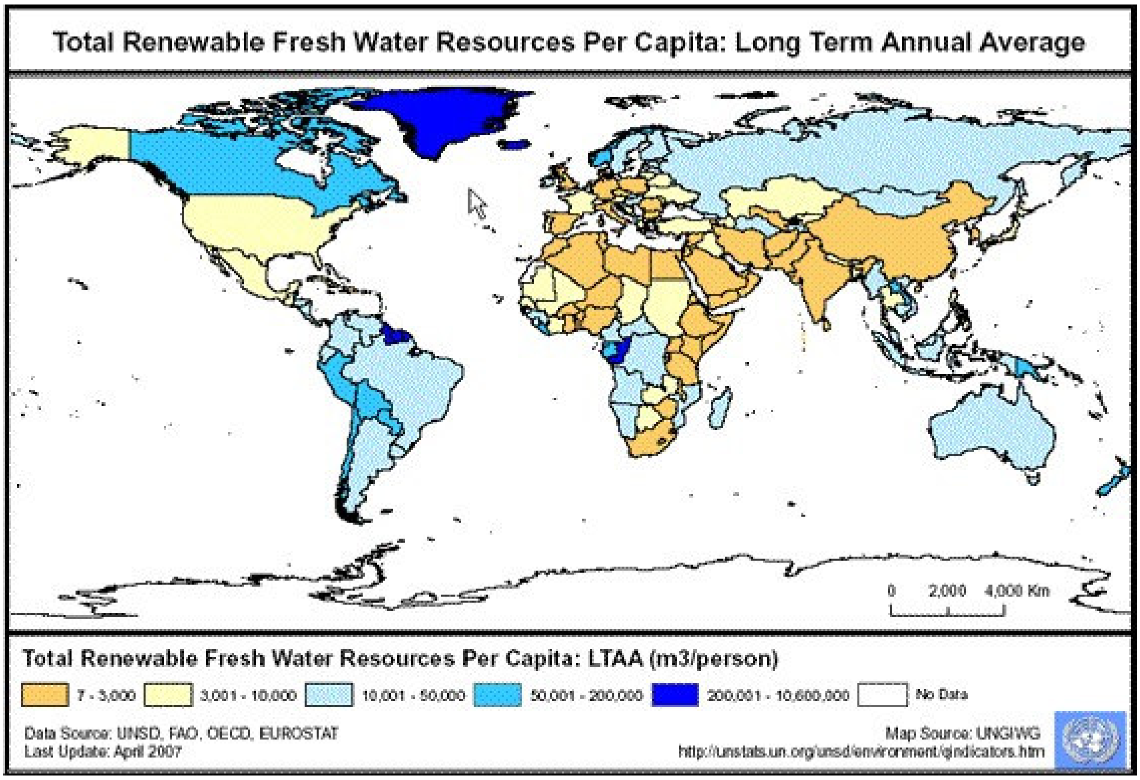

Figure 1.1.4. Total renewable fresh water resources per capita in World, April 2007.[3]

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[3] United Nations Statistics Division, Environmental Indicators, Water, April 2007.

1.2. Phenolic compounds. Environmental considerations.

The German chemist Friedlieb Ferdinand Runge, first isolated phenol from coal tar in 1834, and he gave it the name karbolsäure (coal-oil acid or carbolic acid), though its composition was not known until 1841. The name carbolic acid can be misleading, as it does not contain the functional group normally associated with organic acids, even though it is slightly acidic. Pure phenol is a colourless or white crystalline solid with a powerful sickly sweet antiseptic odour[4]. Table 1.2.1 lists some properties of phenol whereas Figure 1.2.1 shows its chemical structure.

Table 1.2.1. Physical properties of phenol.

Molecular formula	C_6H_5OH
Molar mass	94.11 g/mol
Appearance	White Crystalline Solid
Density	1.07 g/cm³
Melting point	40.5°C
Boiling point	181.7°C
Solubility in water	8.3 g/100 ml (20°C)
Acidity (pK_a)	9.95

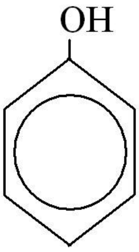

Figure 1.2.1. Phenol molecule.

Phenol is highly corrosive to body tissue, "burning" the skin on contact, though as it also a local anaesthetic, its effect may not be immediately felt. Damage to lung tissue can occur if the vapour is inhaled. Phenol and many substituted phenols are natural components of many substances (e.g. tea, wine and smoked foods), and it is also emitted from the combustion of fossil fuels and tobacco[4].

Phenol was first manufactured commercially by distillation from coal tar, but the energy required and quantities produced meant this method could not be sustained. Synthesis by the sulphonation of benzene was implemented and continued until the 1960s. The sulphonation route produced large quantities of waste and used aggressive reagents, so that several other methods, mostly using benzene as the starting point, were developed. The main method used to manufacture phenol since the 1960s has been through the

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[4] http://www.greener-industry.org/index.htm

oxidation of 1-methylethylbenzene, commonly called cumene, which is made from benzene. Starting with benzene and propene, the whole process includes three steps, with the only other major product being propanone (acetone). Although there is a market for propanone as a solvent, demand for phenol is rising faster than demand for propanone[6].

1.2.1. Uses

Phenol has antiseptic properties and was first used as antiseptic in surgery, although the skin irritation caused by continual exposure to phenol eventually led to stop the use of this compound.

It is also used in the production of drugs (e.g. it is the starting material in the industrial production of aspirin), weedkiller, and synthetic resins (e.g. Bakelite, one of the first synthetic resins to be manufactured, which is a polymer of phenol with formaldehyde).

Phenol is widely used for the manufacturing of products used in our everyday lives. Plywood, window glazing, DVDs and CDs, computers and sports equipment are some of the many items that rely on this important raw material. Phenol is a major component of the phenolic adhesives used in wood products. It is also used to produce phenolic resins, which are used in the moulding of heat-resistant components for household appliances, counter-top and flooring laminates, and foundry castings. In addition, it is a valuable intermediate in the manufacture of detergents, agricultural chemicals, medicines, plasticisers, and dyes (Shell Chemicals, Phenol, 2006).

The largest single market for phenol is in the production of Bisphenol A (BPA), which is manufactured from phenol and acetone. BPA is, in turn, used to manufacture polycarbonate (the largest and fastest growing use for BPA) and epoxy resins. Both polycarbonate and epoxy resins are used in many different industries and in countless items which can be encountered every day like CDs, circuit boards and fibre glass boats (Shell Chemicals, Phenol, 2006).

Global BPA consumption increased at an average yearly rate of almost 10% from 2003 to 2006, driven by polycarbonate demand and also by a significantly improved epoxy resins market in 2006. Polycarbonate resins are both the largest and the fastest-growing end use for BPA and its demand in this market is expected to grow at an average annual rate of 7-8% during years 2006 to 2011[5]. If BPA world consumption is expected to increase in the following years, this will bring as a consequence an increase in phenol demand. In 2004, global production of phenol was nearly 8 million metric tons[6]. Production of BPA consumed 40% of them, followed by phenol-formaldehyde (PF) resins, which consumed 30%. From these data, it is then expected that by year 2011 the world production of phenol could be around 13.8 million metric tons, an increase of 73% in only 7 years. Table 1.2.2 summarises some main commercial derivatives from phenol.

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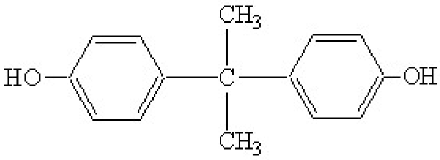
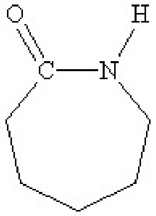
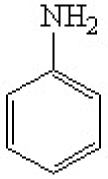
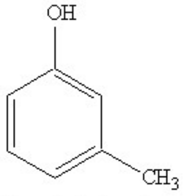
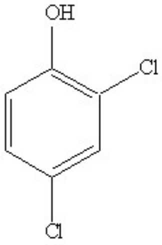
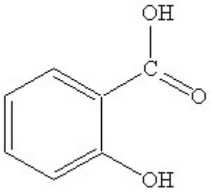
[5] Chemical Economics Handbook, Marketing Research Abstract, November 2007.

[6] Chemical Economics Handbook, Marketing Research Abstract, June 2005.

Table 1.2.2. Intermediates from phenol and the final products obtained.

Derivative	Molecular Structure	Uses
Bisphenol A (GPA)		Used to produce epoxy resins for paints coatings and mouldings, and in polycarbonate plastics, familiar in CDs and domestic electrical appliances.
Caprolactam		Caprolactam is used in the manufacture of nylon and polyamide plastics for a wide range of products, including carpets, clothing, fishing nets, moulded components and packaging.
Aniline		This is used as an antioxidant in rubber manufacture, and as an intermediate in herbicides, dyes and pigments, and pharmaceuticals. It is used to make isocyanates for the production of polyurethanes, with a wide range of uses from paints and adhesives to expanded foam cushions.
Alkylphenols	 3-methylphenol	These compounds are used in the manufacture of surfactants, detergents and emulsifiers, and also in insecticide and plastics production.
Chloro-phenols	 2,4-dichlorophenol	Used in medical antiseptics and bactericides such as TCP and Dettol. Also used in fungicides for timber preservation and as additives to inhibit microbial growth in many products; used to manufacture a range of pesticides
Salicylic acid		Used in the production of aspirin and other related pharmaceuticals.

From: http://www.greener-industry.org/index.htm

As shown in Figures 1.2.2. and 1.2.3, according to the European Pollutant Emission Register (EPER), 500 tons of phenol were emitted directly to water in 2004, and 2177 tons were poured indirectly to water[7] in Europe.

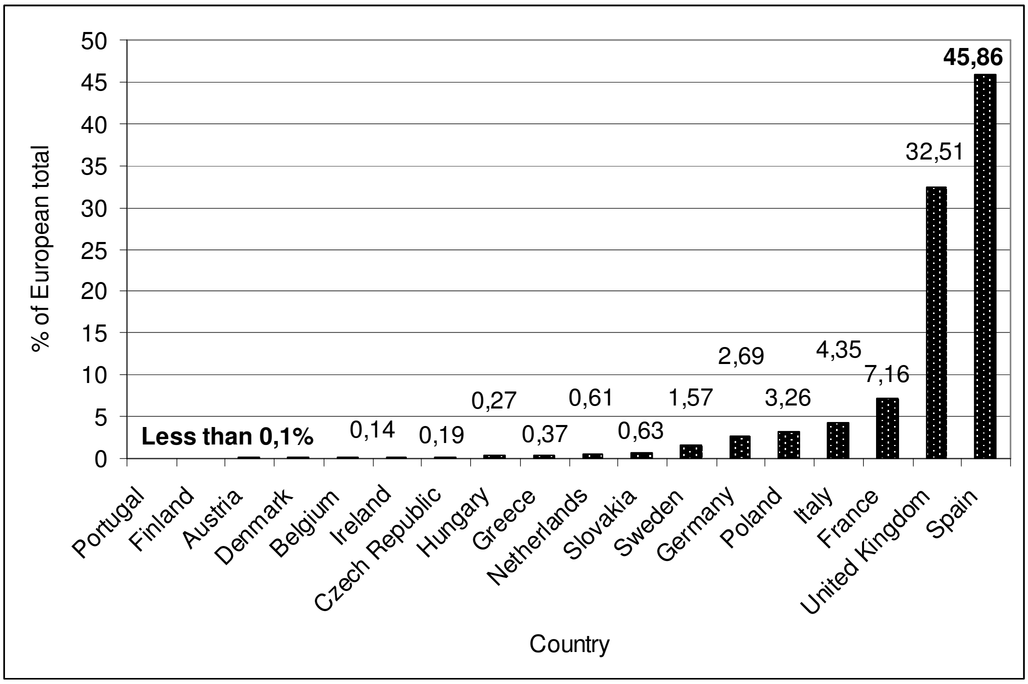


Figure 1.2.2. Phenol emissions direct to water in Europe in 2004, EPER.

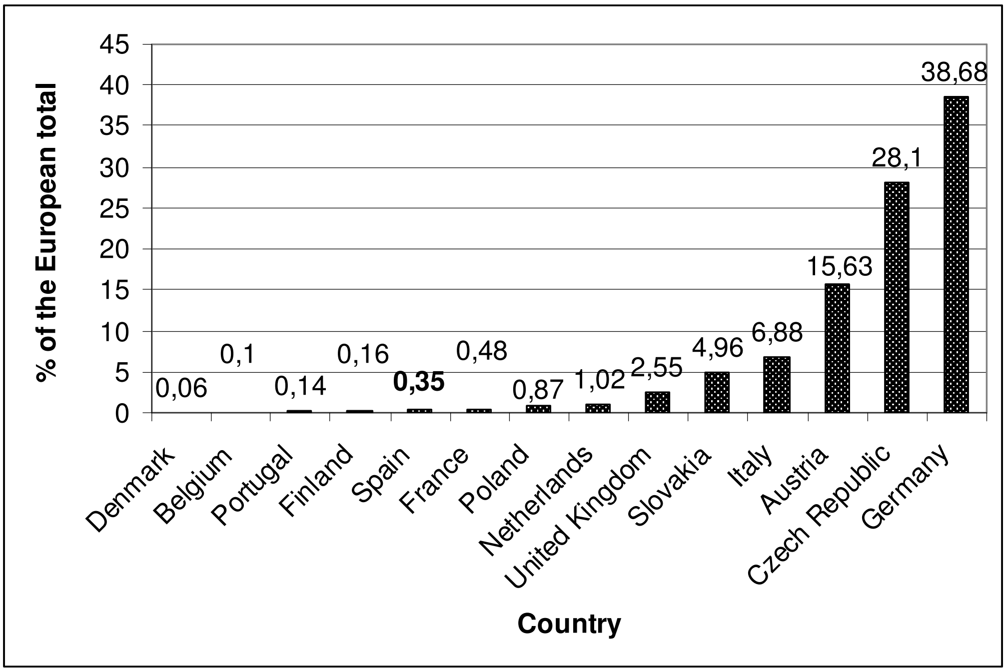


Figure 1.2.3. Phenol emissions indirect to water in Europe in 2004, EPER.

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[7] Values indicated as "direct to water" are emissions by facilities directly into the water environment. Values indicated as "indirect to water" are releases from facilities via a sewer system into an off-site municipal or industrial wastewater treatment plant. In this case, the pollution load is in general significantly reduced.

Figures 1.2.2 and 1.2.3 show that Spain is the first country emissary of phenol directly to water with 229 tons, which represents 45.86% of the total emissions in Europe, and is in tenth place regarding indirect emissions with 7.69 tons, which is 0.35% of the European total. It is worth to note that phenol is a priority substance (EC 1179/94, OJ L131, 26.5.94, p.3.) under Regulation 793/93 (EPER). Phenolic effluents are very common due to the wide variety of industries in which these compounds are used and its main concern arises since they are also toxic and biologically refractory. In conclusion, the high amount of annual phenol emissions makes phenolic effluents a serious environmental issue.

1.3. Wastewater treatments alternatives.

Since the availability of water for next years is seriously compromised, it is necessary to start designing industrial processes that actually avoid and minimise as much as possible the disposal of wastewater. Meantime, it is necessary to deal with wastewater from existent industrial plants. According to Hancock et al. (1999) the main process industries with wastewater concerns are refining, chemical and petrochemicals, pharmaceuticals, pulp and paper, food and municipal wastewater treatment plants. Most of the industries aforementioned have phenolic compounds in their wastewater. Available wastewater treatment technologies can be grouped according to the nature of the treatment in three main groups.

1.3.1. Physical treatments.

Physical treatments include all the methods that involve the application of physical forces, like mixing, flocculation, sedimentation, flotation, filtration, extraction, adsorption and absorption among others (Tchobanoglous and Burton, 1991). The main drawback of these kind of processes is that the hazardous compounds are not actually destroyed and there is need of a subsequent treatment, like the regeneration of the adsorbent which is in most of the cases expensive.

1.3.2. Biological processes.

In this case, the removal of contaminants is achieved by microorganisms. A biological treatment is primarily used to remove biodegradable organic substances (colloidal or dissolved) in wastewater.

Biological treatments are preferred because of the low investment and operating cost required. However, effluents like phenolics cannot be easily degraded and even kill or at least damage the microorganisms responsible for the biological activity. In these cases, conventional depuration cannot be considered anymore, unless a tertiary treatment (physical or chemical) is previously applied to remove the non-biodegradable substances (Tchobanoglous and Burton, 1991).

1.3.3. Chemical operations.

In these methods, the removal of contaminants is made through the addition of chemicals or by chemical reactions, like precipitation and disinfection. The most part of processes are based on the addition of oxidants. Chemical oxidation performance is influenced by pH, temperature, oxidant dosage, reaction time, and the presence of substances that interfere with the desired redox reaction. Typically, rates of chemical oxidation increase with increasing temperature and with increasing oxidant dosage (A.W.W.A., 1990).

Among them, Wet Air Oxidation (WAO) has been used since 1950 to treat industrial effluents. The disadvantage of WAO is that employs high temperature, between 150 and 300ºC, and pressure up to 200 bar. WAO performance can be improved by the addition of homogeneous or heterogeneous catalysts at subcritical conditions. For wastewater containing low to medium pollutant load, Catalytic Wet Air Oxidation (CWAO) yielded satisfactory results in laboratory studies, with the advantage that relatively mild operating conditions can be used, leading to lower investment and operation costs (Stüber et al., 2005).

Suitable catalysts can be used to reduce the severity of the oxidation conditions. Typically, metals like copper, iron, zinc, ruthenium, cerium, etc. have been tested. Mishra et al. (1995) developed several catalysts to improve the liquid phase oxidation of phenol and found that Molybdenum/Cerium composite oxides exhibit much higher activity than even homogeneous copper (Cu) catalyst. They also have studied the catalytic effect of noble metals (Pt, Ru, Rh, Ir and Pd) on WAO of phenol and other important model pollutants. The same behaviour was observed and activities of Ru, Pt, and Rh were higher than that of homogeneous Cu catalyst.

Fortuny et al. (1999a) used Cu oxide over alumina as catalyst in the CWAO of an aqueous phenol solution carried out in a trickle bed reactor (TBR) at mild conditions (up to 160ºC) of temperature and oxygen partial pressure (up to 1.2 MPa). They reached a phenol conversion over 95% and a COD reduction of 90% at 160ºC and 1.2 MPa of oxygen partial pressure. Also Fortuny and co-workers (1999b) developed combinations of mono- and bimetallic alumina supported catalysts (CoO, Fe_2O_3, MnO or ZnO with CuO) to oxidise aqueous phenol solutions using air as oxidant. The conditions used in the TBR were milder than in their previous study (140ºC and 0.9 MPa). The highest conversion was obtained with the CuO-ZnO catalyst, being it about 40%. A decrease in the rate of phenol disappearance with time was observed. It was assumed to be due to the leaching of metal from the catalyst. This is one of the major drawbacks of metal catalysts; they are not enough durable under the typical operation conditions of oxidation processes, i.e. high temperature and acidic environment.

For the CWAO of phenol on a CuO/alumina catalyst, a detailed reaction network was proposed by Eftaxias et al. (2001). 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. The parameters of the model were adjusted using experimental data obtained from a continuous trickle bed reactor using air as oxidant at different temperatures (120-160ºC) and oxygen partial pressures (0.6-1.2 MPa). Simple power law as well as Langmuir–Hinshelwood (L-H) expressions accounting for the adsorption phenomena 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 average deviations below 8%. In addition, all estimated parameters have physical meaning. In particular, activation energies mostly agree with those reported in the literature.

1.4. Activated carbon.

Activated carbon is the collective name for a group of porous carbons, manufactured by the treatment of a char with gases or by carbonisation of carbonaceous materials with simultaneous activation by chemical or physical means. All these carbons are prepared to exhibit a high porosity and internal surface area (Rodríguez-Reinoso, 1997).

Activated carbons can be produced from virtually any carbonaceous solid precursor, synthetic or natural. Process economics normally dictate the selection of readily available, low-cost feedstock. Common examples of commercial feed stocks are materials of vegetal, e.g. wood, coconut shell and nut kernels, or mineral origin, e.g. peat, lignite and all ranks of coal. The most commonly used activated carbons are produced in the needed volumes by relatively straightforward processing methods, and in powdered, granular or performed shapes, e.g. pellets, extrudate (Derbyshire, 1994).

During the first decades of the last century, activated carbon was used for the purification of chemical, pharmaceutical and food industry products. However, purification of drinking water was by far the most important application (Rodríguez-Reinoso, 1997).

The efficiency of an activated carbon depends on its accessible internal surface area and also on the concentration of active sites in the surface. The precursor and preparation methods (and/or possible activation) not only determine its porosity but also the chemical nature of its surface, which consequently establishes its adsorptive and catalytic characteristics (Rodríguez-Reinoso, 1997; Khalil et al., 2001). Despite most of the adsorption takes place in the micropores of the AC, meso- and macropores are also important in any adsorption process, because they serve as passage for the adsorbate to the reach micropores. That is why, in order to obtain the better performance of this material textural and chemical properties should be tuned according to the process it will be used in.

Figures 1.4.1 and 1.4.2 show how the internal structure of activated carbon is and how it is present the different porosity in it. Depending on the molecular size of the adsorbate, it will interact with the macro-, meso- or micropore. However, the chemistry of the activated carbon surface is determinant when considering the affinity of any chemical compound with AC. In Figure 1.4.3, the different types of oxygen surface groups in activated carbon are depicted. The presence of these surface groups gives to activated carbon an acid-base character. Typically, the kind of oxygen functionalities in the surface of AC is caused by the route of manufacturing employed and also by the activation procedure applied.

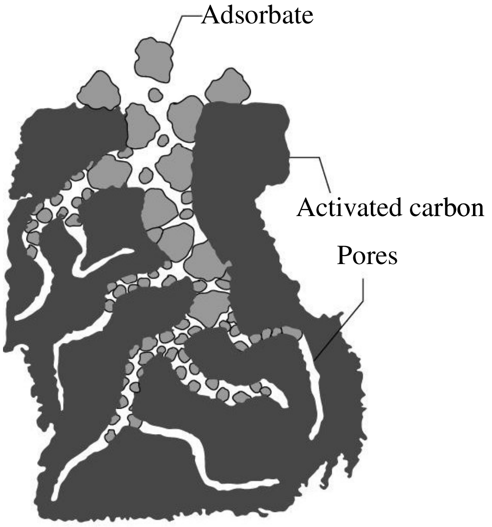


Figure 1.4.1. Internal structure of activated carbon.

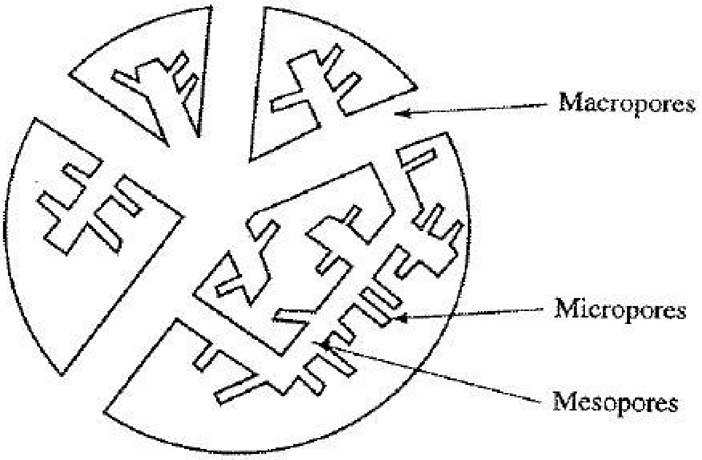


Figure 1.4.2. Porosity in AC (Marsh and Rodríguez-Reinoso, 2006).

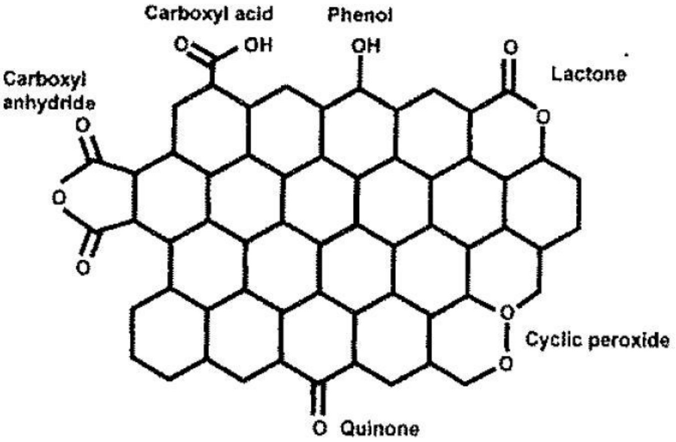


Figure 1.4.3. Types of oxygen groups on AC surface (Rodriguez-Reinoso, 1998).

Another important parameter that affects the characteristics of the AC is the ash content. It can widely vary with the raw material. The ash content may range from 1 wt % for AC prepared from relatively pure raw materials to more than 10% in AC made from coal. The different possible components of the ash (silicates, aluminosilicates, calcium, magnesium, iron, potassium and sodium oxides) are important in adsorption processes, since they modify the interaction between the AC surface and the adsorbate. Also, this mineral matter may have catalytic effect in the gasification reaction during activation (Marsh and Rodríguez-Reinoso, 2006).

1.4.1 Activation procedures

There are two principal methods for manufacturing AC's known as physical and chemical activation. Physical activation is a two step process that comprises carbonisation of the raw material in an inert atmosphere followed by partial gasification of the resulting char with steam, CO_2 or a mixture of them. Evolution of microporosity is relatively similar for those two activating agents. Further gasification results in a decrease in micropore volume for the case of CO_2. Steam produces a continuous increase with burn-off, which indicates enlargement of micropores and their size shift towards mesopores. In chemical activation, the two steps involved in activation are carried out simultaneously. The raw material is impregnated by a compound such as H_3PO_4 or $ZnCl_2$, the impregnated product is pyrolysed and then washed to remove the activating agent. Chemical activation is usually carried out if the raw material is wood or peat. In this case, there is dehydration of the cellulosic material during pyrolysis, which results into charring and aromatisation of the carbon skeleton, and the creation of the porous structure. All chemicals are dehydrating agents and inhibit tar formation. The yield of the process is relatively large, i.e., it may exceed that of the physical activation method by up to 30% wt. Other possible advantages of chemical activation are: (a) simplicity, no need of previous carbonisation of raw material; (b) lower temperatures of activation; and (c) good development of the porous structure (Dabrowski, 2005). Figure 1.4.4 shows a basic scheme for the two methods of activation.

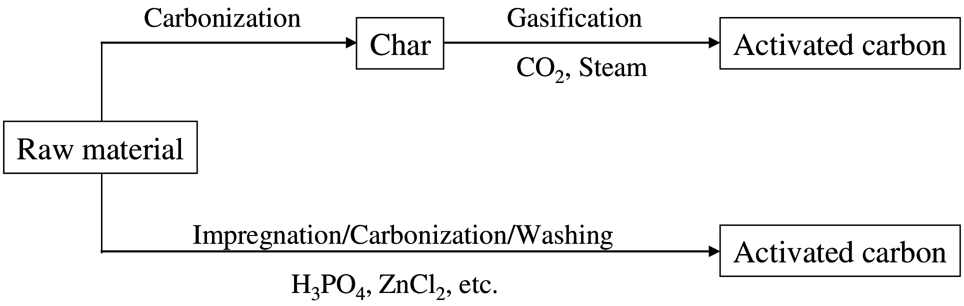


Figure 1.4.4. Basic scheme for the two methods of activation.

Although the activated carbons obtained by chemical activation have a well developed porosity, the porous structure can be modified by further activation with CO_2 or steam, this resulting in the preparation of activated carbons with very high surface area compatible with reasonable bulk density (Marsh and Rodríguez-Reinoso, 2006).

An additional one step activation route denoted as steam-pyrolisis has been reported. In this case the raw material is heated either at moderate or high temperatures (500-800ºC) under a flow of steam and the final temperature is kept for a short period of time under the steam flow. This type of activation produces a larger development of porosity than that from activation with steam of material carbonised in nitrogen (Ioannidou and Zabaniotou, 2007).

As above mentioned, the ash content of the raw material affects the gasification reaction during physical activation. Components like iron and calcium exhibit different catalytic effect during gasification. They cannot only modify the gasification rate, they also influence the development of selective pore formation. It has been proposed that metals like iron and potassium promote the formation of micropores, whereas calcium and transition metals enhance mesopore formation (Marsh and Rodríguez-Reinoso, 2006).

1.4.2. Applications.

1.4.2.1. Adsorption.

AC's are typically used as adsorbent in numerous physical separation processes, including water and air treatment. AC is able to adsorb almost any kind of organic and inorganic compounds due to its heterogeneous surface. Adsorption of phenolic compounds in liquid phase is being studied for long time and it is now very well characterised. In the 1960s, Mattson et al. (1969) identified by IR the main oxygen surface functional groups in a commercial lignin based AC in order to establish a relationship between the surface oxygen content and the adsorption capacity towards organic compounds (phenol, meta- and para-nitrophenol and nitrobenzene). They postulate that the adsorption of phenol is mostly influenced by the interaction of the aromatic ring with the surface of the AC through the formation of donor-acceptor complexes. This mechanism involves carbonyl oxygen groups acting as electron donor, and the aromatic ring of phenol acting as acceptor. It has been also proposed that other oxygen functionalities like carboxyl and hydroxyl inhibited the adsorption of phenol and increase the affinity of the carbon towards water (Coughlin and Ezra 1968, referenced in Mattson et al., 1969, and Dabrowski at al., 2005). Terzyk et al. (2003) named this "the solvent effect" and can occur when at infinite dilution and neutral pH, the positive surface charge resulting from the adsorption of protons by the strongest surface bases leads to the increase in water adsorption and blocking some of the most active sites for the adsorption of phenol. Other interaction has been also proposed for the adsorption of aromatic compounds over AC. It has been called the π-π interactions and it assumes that there are dispersion interactions between the π electrons of the basal plane of carbon and the aromatic ring of the adsorbate. This mechanism has been postulated as responsible for the adsorption of phenolics. Despite the adsorption of phenol has been widely studied (Dabrowski at al., 2005; Terzyk, 2003), AC has been largely applied for the adsorption of other aromatics, dyes and even metals.

For instance, Nouri (2002) investigated the adsorption of p-cresol over a commercial AC with different surface oxygen content and found that the adsorption of this compound increases up to 35% when the surface oxygen content is low. Tseng et al. (2005) studied the importance of surface area and porosity distribution in the adsorption kinetics of several compounds like 2,4-dichlorophenol and 4-chlorophenol on AC prepared from corncob, obtaining very good adjustments and very good values of adsorption capacity. In 2006 (Tseng et al., 2006a; Tseng et al., 2006b), they also test the adsorption of p-nitrophenol, p-chlorophenol and p-cresol among others compounds on AC prepared from cane pith by KOH activation and from corncob activated by KOH plus CO_2 gasification. In this paper they also calculate the Elovich equation parameters for the adsorption of the mentioned compounds achieving relatively high adsorption capacities and very suitably fitting. Suárez-Ojeda et al. (2005) also studied the adsorption of o-cresol and 2-chlorophenol over a commercial AC, obtaining very good results and good adjustment to Freundlinch equation. Lillo-Ródenas et al. (2005) used activated carbon with different pore size distribution and different surface oxygen group content for benzene and toluene adsorption in gas phase. They concluded that the two parameters studied have great influence on the adsorption of these compounds, the porosity being the most important. However, the authors observed that, when AC has a low content of surface oxygen functionalities, it shows higher adsorption capacity for both benzene and toluene. The competitive adsorption of a mixture water-toluene on AC was evaluated by Heinen et al. (2000) concluding that the more acidic the surface of the carbon, the more hydrophilicity exhibited, increasing the adsorption capacity towards water. Other mixture like phenol-aniline has been studied by Nevskaia et al. (2004) and Lászlo (2005). Both studies highlight the importance of the surface chemistry of the AC and in general both conclude that the presence of acidic oxygen groups displaces the selectivity towards the uptake of the more basic adsorbate. Related with the pharmaceutical industry, the adsorption of phenol and salicylic acid was studied by Ania et al. (2002, 2004). Results from these works demonstrate that whereas the adsorption of phenol over AC is more influenced by the surface chemistry of the adsorbent than by its porosity, the retention of salicylic acid is more related to the texture of AC than to its surface chemistry.

Other organic compounds have been also adsorbed over AC. Considine et al. (2001) studied the adsorption of 2-methylisoborneol (MIB) from aqueous solution on two vegetal based AC. MIB is one of the most common taste and odour molecules found in water. Its molecular structure consists of a hydrocarbon skeleton containing one hydroxyl group and thus, it is considered a relatively hydrophobic compound. Their results were in agreement with what has been stated by other researchers: the less the amount of surface oxygen in the AC, the less its hydration in aqueous solution, thus facilitating the MIB adsorption. García et al. (2004) studied the adsorption of phenanthrene (Phe) over a commercial AC. Phe is a compound of the family of polycyclic aromatic hydrocarbons, which are important environmental pollutants. Their results support what has been stated before, an increase in the polar character of the AC produces a decrease in the Phe adsorption. All carbon samples used in this work have similar porosity, so the impact of this parameter was not evaluated in the adsorption performance of this compound. Humic acids (HAs) are natural polyelectrolytes that have harmful effect on the water quality (bad colour and taste) and serve as food for bacterial growth. In addition, they react with chlorine during water treatment producing chlorinated organic compounds, which can potentially be human carcinogens and impart a disgusting taste. Mesoporous AC was successfully used by Lorec-Grabowska and Gryglewicz (2005) for the elimination of these undesirable compounds from water. In this case due to the better developed mesoporosity that acts as a transporting artery, the carbons used show a good ability to adsorb HA’s. In the food industry, a commercial AC has efficiently removed Ochratoxin A from artificially contaminated phosphate-buffered saline and white wine (Var et al., 2008).

Another field where AC is widely used is for the adsorption of dyes. San Miguel et al. (2002) compared the performance of AC made from waste tyre rubber by physical activation with steam and two commercial carbons in the adsorption of methylene blue, and textile dyes, i.e. Turquoise H-A and Red H-E2B. The adsorption capacity of the tyre rubber carbons was in all cases superior to that of the commercial carbons, being up to ten times higher for the Turquoise H-A and Red H-E2B and two folds for the methylene blue. Rio et al. (2005a,b) used AC made from sewage sludge for adsorption of two organic dyes, i.e. acid red 18 and basic violet 4. In this case, the mesopore volume is the most important texture parameter in the adsorption of basic and acid dyes. Kumar et al. (2006) manufactured an AC from rubberwood sawdust and used it in the adsorption of Bismark Brown dye, obtaining an adsorption capacity five times higher than that obtained with a commercial AC (1250 vs. 250 mg/g AC).
Another application of activated carbon is in the raw sugar decolourisation. Ahmedna et al. (1997) manufactured an AC from agricultural by-products and successfully used them in the decolourisation of one standard test liquor. Hence, the decolourisation capacity of an AC made from rice hulls was comparable with a commercial one from Calgon, 80% of decolourisation for both. Mudoga et al. (2008) also used carbons made from agricultural by-products, beet pulp in this case, in the sugar syrup decolourisation, obtaining very good results and also comparables with those obtained using two commercial carbons, 70% of decolourisation vs. 80% obtained with those commercial.

Metal ions can also be removed from liquid effluents with activated carbon. Heavy metal ions like Pb, Cr and Cd were efficiently removed by Park et al. (2002) with a commercial AC treated with HNO_3, up to 100% of removal in the case of Pb, 90% for Cd and 25% for Cr. Arsenic has also been adsorbed on AC by Gu et al. (2005). In this case, AC was first impregnated with iron to improve the arsenic removal. The adsorption capacity of the modified samples was approximately 1000 times higher than the capacity of the commercial parent AC.

In summary, AC can be used for the adsorption of a wide variety of organic compounds. In most cases the key parameters are AC textural properties and surface chemistry. However, an appropriate surface chemistry that allows the best interaction between the adsorbate and the carbon seems to be determinant for the better performance of this material.

1.4.2.2. Metal support.

AC is a recognized catalytic support due to the unique characteristics such as tuneable textural properties, erosion resistance and surface chemistry. Another advantage is its chemical stability in acidic and basic media. In addition, if valuable, metals want to be recovered, AC can be burned and metals accumulate in the ashes (Stüber et al. 2005).

The two most important aspects of the carbon that should be consider when using carbon as a metal support are the surface area and porosity, and the surface chemistry. High surface area and well developed porosity are essential for achieving large metal dispersions, which usually results in a high catalytic activity. Regarding the surface chemistry, although carbon is considered to be an inert material in comparison with other catalyst supports such as alumina and silica, its surface has a proportion of active sites constituted by unsaturated valences at the edges of the graphene layers formed by inert carbon atoms. The presence of heteroatoms (mainly oxygen and nitrogen) also introduces active sites on the carbon surface, and consequently the carbon surface is not as inert as it could be expected. Particularly, oxygen surface groups are of the greatest interest in the preparation of carbon supported catalysts, since the common methods of excess-solution and incipient-wetness impregnation or ion-exchange entail contacting the carbon with a solution of the catalyst precursor (Rodríguez-Reinoso, 1998).

Duprez et al. (1996) supported Ru, Pt and Rh on cerium dioxide, titanium dioxide and activated carbon and use them as catalyst in the WAO of acetic acid. The Rh/C catalyst has the best performance in the oxidation of acetic acid, giving COD removal of 97% after 3 hours, despite there was evidence that the carbon support was partially oxidised into CO_2 during operation. Calafat et al. (1996) used Ni and Mo immobilised on two different commercial AC for the thiophene hydrodesulfurisation (HDS) and compared it catalytic behaviour with a NiMo catalyst supported on alumina. The NiMo catalyst based on AC made from lignocellulosic raw material by physical activation show a catalytic activity one and a half times higher than that supported on AC made from the same raw material by chemical activation, and three times higher than the catalytic activity shown by the NiMo/alumina catalyst. The difference in activity is attributed to the different textural properties of the different AC, since the carbon made by physical activation has higher microporosity than that made by chemical means. Hu et al. (1999) supported Cu as active metal on a commercial AC from Norit for oxidation treatment of a dyeing and printing wastewater from a textile company. The COD and TOC reduction of the wastewater was higher with the Cu/AC catalyst than with the catalyst made with the same metal supported on alumina or with the homogenous catalyst, copper nitrate in solution, i.e. reduction of 91% of COD and 64% of TOC. Gomes et al. (2000) used a carbon supported Pt catalyst to study the CWAO of low molecular weight carboxylic acids as model compounds. Their results showed that, at around 200ºC and at 7 bar of oxygen partial pressure, a very high catalytic activity is obtained, with a selectivity to gaseous products and water near 100%. Trawczynski (2003) developed Pt, Pd and Ru catalysts supported on carbon black composites (CBC) for the oxidation of phenol solutions using a fixed bed reactor operating in trickle-flow regime. All catalysts were efficient, achieving almost complete conversion of phenol at temperatures higher than 140ºC. Also, Álvarez et al. (2002a and 2002b) and Wu et al. (2005) used copper supported activated carbons as catalysts in the catalytic oxidation of phenol, and despite good phenol conversions were achieved in their studies, the copper leaching was responsible for deactivation in both cases. Quintanilla et al (2006) supported iron on a commercial AC and used this catalyst in the wet air oxidation of phenol. The oxidant agent used was pure oxygen and the study of the intermediates products formed was also studied.

1.4.2.3. Catalyst. Use of AC in CWAO.

Several decades ago, Coughlin (1969) pointed out that since AC may display electronic properties of conductor, semiconductor or insulator, it may act as catalyst in several reactions like hydrogenation, oxidation and polymerisation. The currently most important industrial use of AC as catalyst is for the production of phosgene, followed by oxidation of harmful gases such as SO_2, NO and H_2S in air pollution control (Stüber et al., 2005). However, it is not until recent years that applications of AC as catalyst in liquid phase have been reported. According to Stüber et al. (2005), the lack of studies of carbons as catalysts is due to the few applications of these materials had in oil refining and petrochemical industries, which typically lead the research in heterogeneous catalysis. But with the recent applications of carbon as catalyst in fuel cells, environmental and fine chemical, a better understanding of the behaviour and properties of its catalytic capacity is needed.

In 1998, Fortuny et al. (1998) and Tukac et al. (1998) proposed to use activated carbon directly as catalyst in CWAO of phenol, in batch and in a trickle bed reactor configuration with excellent results. Fortuny et al. (1998) worked with a commercial AC that gives higher phenol conversion than a commercial oxidation catalyst based on copper. The latter undergoes a rapid deactivation by losing the copper active species as a consequence of its poor stability in the hot acidic aqueous medium. In turn, the active carbon, without the presence of any active metal, demonstrated to have catalytic effect on the wet oxidation of phenol operating at mild conditions of pressure, i.e. oxygen partial pressure 0.9 MPa, and temperature, 140ºC, in a fixed bed reactor operating in trickle flow regime. However, a continuous fall of phenol conversion during the test was observed, which went from 100% at the beginning down to 48% after 10 days of operation. Despite operating at mild conditions, at the end of the run, it was found that 33% of the initial carbon had been consumed. This suggests that, the decrease of catalytic efficiency with time could be due to carbon consumption and its subsequent loss in surface area.

Tukac et al. (1998) worked at similar conditions than Fortuny et al. (1998), i.e. total pressure of 2-5 MPa, and temperature in the range 110-160ºC, with a slurry configuration and also in a trickle bed reactor with an active carbon black and a charcoal. Both tested catalysts exhibited oxidation activity. The rate of substance disappearance was proportional to its concentration. They also established a proportional relationship between reaction rate of phenol oxidation and oxygen concentration.

During the last decade, the use of activated carbon as catalyst for CWAO has gained more and more attention. Fortuny et al. (1999c) performed CWAO of phenol in a trickle bed reactor using three different commercial activated carbons as catalyst. The main difference between all carbons was the raw material -hence the mineral content was also different- used for the manufacture of the AC. The reactor operated at 140ºC and the oxygen partial pressure was varied from 0.1 to 0.9 MPa. First, an analysis of the impact of the oxygen partial pressure in the phenol oxidation was done using one of the commercial AC from Merck. Several interesting observations can be made from the results obtained. During the first 24 hours of operation the process is dominated by an initial adsorption step since no phenol is observed in the exit stream. Beyond 24 hours, the conversion of phenol considerably decreased with time when using 9 and 4 bar of oxygen partial pressure. This indicates significant carbon consumption during operation. On the contrary, almost constant phenol conversion was found at 1 and 2 MPa, which indicates low carbon consumption. At the end of each test, the change of AC mass was measured, obtaining the lower value when operating at 2 bar, only 3% more. This increase in the AC final mass could be due to the deposition of phenol-based polymer-like species, products of the oxidative coupling reactions that take place inside the reactor. Another interesting observation is that, despite the final phenol conversion decreases with the decrease of the oxygen partial pressure, the selectivity to CO_2 in all cases was around 73%, which reveal a very low dependence of selectivity with this parameter. The difference between the phenol conversion obtained at 0.9 MPa and

2 MPa was only 10% (45% vs. 35% respectively). For this reason the comparison of the performance of the three commercial AC was done operating at 2 bar of oxygen partial pressure. During the first 24 hours, there was an apparent 100% conversion due to the adsorption of phenol on the AC. Once the pseudoequilibrium was reached, a steady phenol conversion was obtained. The final conversion obtained with the three commercial AC was dramatically different from each other. The best performance is given by ME with 35% of phenol conversion after 10 days of operation. One carbon made from mineral source and with high ash content (PJ) rendered 15% and with the last carbon made from coconut (GH) only 8% was obtained. The authors concluded that neither the mineral matter nor the pore volume can be totally related to the phenol conversion. Samples ME and GH have similar ash content (related to the mineral matter): 4% and 3% respectively, and its catalytic activity were not comparable. They also stated that textural properties may have an impact in the catalytic behaviour, despite its effect cannot been seen clear from the results obtained.

CWAO of phenol was performed for comparative purposes in a slurry and trickle bed reactor (TBR) by Stüber et al. (2001) using AC as catalytic material. At operation conditions in the slurry reactor of 160ºC and 0.71 MPa, almost compete phenol removal was achieved. When compared with the TBR (140ºC and 0.55 MPa), slurry system gave extremely faster initial rates of phenol destruction. However, the oxidation of phenol towards intermediates and CO_2 was strongly enhanced in the trickle system. The authors proposed than the slurry system promotes the formation of heavy polymers, which irreversible adsorb on the AC surface, decreasing its catalytic activity by a sort of deactivation. In the TBR system, the high catalyst to liquid ratio favours the heterogeneous oxidation rather than the phenol condensation reactions.

Recently, Suarez-Ojeda et al. (2005) used CWAO over several phenolics compounds, i.e. phenol, o-cresol, 2-chlorophenol and p-nitrophenol, as a suitable precursor for the biological treatment of industrial wastewater using a commercial AC as catalyst and operating in a TBR. The AC used proved to be effective for the oxidation of 2-chlorophenol (55% of conversion), phenol (45%), o-cresol (33%) but showed practically no conversion for p-nitrophenol. The data from COD and TOC conversion demonstrated that the depth of the oxidation depends on the properties of the compound. The experimental reactivity order was 2-chlorophenol > phenol > o-cresol, and it can be explained by the type of the aromatic substitution. Chloride is a strongly activating nucleophilic aromatic substituent, whereas hydroxyl and methyl are deactivating groups. Therefore, the theoretical oxidation easiness of the compounds matched with the experimental results.

Eftaxias et al. (2005) studied the kinetics of phenol oxidation in the TBR over AC as catalyst operating in temperature and oxygen partial pressure ranges of 120-160ºC and 0.1-0.2 MPa. The kinetic analysis showed that both simple power law model and more mechanistic Langmuir-Hinshelwood models can accurately predict the entire experimental results. The reliability of the kinetic model developed in that study could be a useful tool for the scale-up and modelling of TBR's applied to CWAO technologies.

Other researchers have also used AC as catalyst in the CWAO of phenol. Santos et al. (2005) used three commercial AC in a fixed bed reactor at 160ºC and 1.6 MPa of oxygen partial pressure. Their results are in agreement with what has been previously reported by Fortuny et al. (1998), Stüber et al. (2001) and Suárez-Ojeda et al. (2005), obtaining high phenol mineralisation for up to 60 hours.

However, and despite there are many studies concerning the use of AC as catalyst in the CWAO of phenol, the parameter responsible for this catalytic behaviour has not yet been well identified. However, the AC surface chemistry is determinant when evaluating the adsorption capacity of this material. Using the appropriate techniques and methodologies, the surface functionalities or textural properties of AC can be modified in order to obtain a material with specific properties oriented to improve its interactions with a certain compound, which could have impact on the catalytic performance in CWAO. In the next section, the most common modifications made on AC are summarised, including those which are aimed to clarify the parameters responsible for the catalytic activity of AC.

1.4.3. Modifications on AC.

In general, modifications on AC can be made in gas or liquid phase. Typically, inert gases like nitrogen, helium or argon can be used in thermal treatments to modify the surface chemistry by removing oxygen functionalities. This procedure allows to have a more clean carbon surface, which improves the interaction of some organic compounds, e.g. aromatics with the aromaticity of the carbon thus increasing the adsorption capacity.

For instance, Tessmer et al. (1997) outgassed several commercial AC in argon atmosphere at different temperatures, changing the surface functional group content and later they evaluated their effect on the adsorption capacity of phenolic compounds. The AC outgassed at 500ºC showed a greater capacity for the adsorption of 2-chlorophenol, due to the removal of acidic groups. Raising the outgassing temperature also promotes the re-formation of basic groups and this increase the adsorption capacity.

Some of the works discussed in the section dedicated to the use of AC in adsorption (section 1.4.2.1) made gas phase treatments on the carbon studied to evaluate the impact of this parameter in the adsorption capacity studied in each work. Lillo-Ródenas et al. (2005) improved the adsorption of benzene and toluene in gas phase. They thermally treated the activated carbon. Thus, the surface oxygen content was reduced, whereas the porosity and surface area remained nearly unchanged. Subsequently, it was demonstrated that benzene and toluene are preferentially adsorbed over graphitic carbon.

Considine et al. (2001) improved the adsorption of MIB when a heat treatment under argon was conducted on the AC used in their study. Nevskaia et al. (2004) studied the impact of surface oxygen content in the adsorption of phenol, aniline and phenol-aniline mixtures on a carbon from Norit treated at 900ºC under a flow of helium. They found that the decrease of oxygen groups increases the adsorption capacity and, in the case of a mixture, displaced the selectivity towards the more acidic compound.

Dastgheib et al. (2004) and Chen et al. (2005a) treated commercial AC under anhydrous ammonia at different temperatures. In both cases, the treatment was effective in changing the microporosity when conducted at temperatures higher than 500ºC, whereas 400ºC seemed to be enough to improve carbon surface basicity by neutralising surface acidities. Modifications product of this ammonia treatment favoured the adsorption of dissolved organic matter (Dastgheib et al., 2004) by improving the interaction of the carbon surface with the organic matter and by increasing the accessible surface area available for adsorption. Also Chen et al. (2005b) improved the adsorption of perchlorate from aqueous solution after ammonia thermal treatment. Przepiorsky (2006) evaluated the phenol adsorption capacity of three commercial AC after heat treatment under ammonia at 400, 600, 700 and 800ºC. In comparison with the untreated material, each activated carbon modified demonstrated enhanced adsorption capacity towards phenol, being the highest improvement for those activated carbons treated at 600-700ºC (up to 30%).

Treatments in liquid phase are typically made with strong acids, such as nitric or sulphuric acid among others. When AC is oxidised in acid, an increase in the surface oxygen content is expected, mainly due to the formation of acidic functionalities. As above explained, the increase in oxygen in the carbon surface makes it more hydrophilic, increasing its affinity toward water. This produces a decrease of the adsorption capacity when trying to adsorb aromatic compounds. This was evidenced in several studies (Heinen et al., 2000; Nouri, 2002; Ania et al., 2002, 2004; El-Hendawy, 2003; García et al., 2004; Dastgheib et al., 2004; Faria et al., 2008). They reported a decrease in the adsorption capacity of aromatics such as toluene, p-cresol, phenantrene, aniline, sulfanilic acid, benzenesulfonic acid and phenol after making an acid treatment on the AC. Depending on the severity of the treatment, textural properties can be strongly modified.

The widening of the porosity can be observed in some cases as a consequence of the oxidation of the edges of the carbonaceous matrix, decreasing the microporosity volume and increasing the mesoporisity. This effect could be useful in some cases, for instance for the adsorption of large molecules that cannot reach the micropores. Jiang et al. (2003) modified by oxidation treatment with concentrated sulphuric acid (96%), at temperatures up to 270ºC and 3 hours of exposure, a commercial AC. The sample treated at 250ºC showed an increase of 86% of mesopore volume, of 90% in the surface area, and the acidic surface functionalities increase up to 28 times the original value. These modifications enhanced the adsorption of large molecules like methylene blue (MB) and dibenzothiophene. As expected, the affinity toward chlorophenol and iodine lowered considerably, i.e. a decrease in the adsorption capacity of 45% and 72%, respectively. Tan et al. (2008) also reported an increase of 24% on the MB adsorption capacity of a vegetal based carbon after treatment with HCl.

Another interesting application of the increase in acidity of the AC surface is for metal recovery. Typical acidic surface functional groups (see Figure 1.4.3) are essential for the adsorption of heavy metals due to its chelating properties, where metal cations can be integrated with the groups to form complexes as indicated in the following equation (Yang et al. 2007):

$$M^{n+} + n(\text{-COOH}) \leftrightarrow (\text{-COO})nM + nH^{+} \qquad \text{Eq.1}$$

The above reaction occurs due to a cation exchange mechanism where the cation replaces the hydrogen ion previously attached at the whole carboxylic group.

For instance, Torres et al. (1997) treated a commercial AC with HNO_3 and weak oxidants like H_2O_2 and O_3, to test the effect of oxidation in its performance as support for Pt catalyst. The HNO_3 treatment produced a high concentration of strong acidic sites, while H_2O_2 and O_3 only enhanced the formation of weak acidic groups, which show strong interaction with H_2PtCl_6 in the impregnation stage, this favoured the Pt dispersion on the carbon surface and consequently the catalytic behaviour. Park et al. (2002) treated a coconut based commercial AC with HCl and tested the modified samples in the adsorption of Cr(IV) obtaining an increase in the adsorption capacity of near 25% compared with the untreated carbon, while only slight increase in surface area and microporosity was reported. Rios et al. (2003) oxidised a commercial AC from Norit with concentrated nitric acid four times between 2 and 38 hours. After 38 hours refluxing in the acid, the AC weight loss was about 45%. On the other hand, thermogravimetric analysis results demonstrated that there is no significant difference between the sample treated for 16 hours when compared with that oxidised for 38 hours, which indicates that the formation of acidic groups reached a maximum at certain time and remain constant beyond that. The HNO_3 treatment dramatically increases the adsorption of cations like Pb^{2+}, up to 18 times (from 4 mg/g AC to 70 mg/g AC), and Cd^{2+}, up to 5 times (from 5 mg/g AC to 25 mg/g AC). Finally, in the review of Yang et al. (2007), up to 19 citations can be found where acidic treatment was successfully used for increasing the acidic functionalities on AC surface, positively impacting the removal of metal ions, too.

Other compounds, for instance metal oxides, can be previously adsorbed on AC in order to improve its subsequent adsorption performance. Mei et al. (2008) prepared three loaded AC with $Mn(NO_3)_2$, $Co(NO_3)_2$ and $CuCoO_4$. These modified samples were used in the adsorption of gas phase Hg^0. Metal loaded carbons showed better performance than that of the parent AC. However, samples treated with Mn and Co showed to be easily poisoned when SO_2 was present in the gas stream. Instead, the sample treated with $CuCoO_4$, showed a convenient anti-poisoning ability, making this materials useful for the Hg^0 elimination from gas phase. Çelik et al. (2008) improved the performance of a commercial AC in the removal of boron in aqueous solution by prior impregnation with salicylic acid. This effect is attributed to the formation of a cyclic molecule between -OH and -COOH ends of the salicylic acid impregnated on the carbon with the boric acid molecule. Fortier et al. (2008) applied the impregnation of $ZnCl_2$ on a coconut shell based AC and improved the adsorption capacity towards gaseous NH_3.

An interesting application of metal impregnation is for the modification of porosity in carbons. Particularly Ca and Fe load has been proposed as an effective pre-treatment to produce mesoporous activated carbons by gasification of impregnated precursors. Lorenc-Grabowska et al. (2004) increased the mesoporosity of a lignite based AC by impregnating just Ca, and Ca and Fe before the carbonisation and activation step. The mesopore volume was five times higher, when the impregnation was done with the two metals, and more than three folds higher, when using just Ca, than the mesopore volume obtained if the AC was activated without any impregnation. Rio et al. (2005a) also increased the mesopore fraction of the porosity on an AC made from sewage sludge when lime was added before the activation step. Qiao et al. (2005) impregnated Fe instead of Ca in a commercial AC already activated, making a later gasification under CO_2, thus achieving an increase in the mesopore volume of three times the original value.

More directly related to the use of AC as catalyst, Pereira et al. (1999) modified by means of oxidative treatments in both gas and liquid phase a commercial activated carbon. Later, they tested the modified AC's as catalysts in the oxidative dehydrogenation of ethyl benzene (ODH). Both types of oxidation treatment led to an increase in the amount of surface oxygen groups; but the gas phase treatment was more effective than the liquid phase oxidation for increasing the amount of carbonyl/quinone groups on the surface of the catalyst. Then, by a thermal treatment applied to an oxidised sample, some of the functional groups were selectively removed. They observed that these treatments did not change the texture of the carbon. Finally, the catalytic activity tests showed that gas phase treatments significantly improved the performance of the catalyst in ODH. Also the conversion was not significantly affected by thermal treatment up to 750ºC, but after treatment at 1100ºC it abruptly dropped to the levels observed with the original carbon previously oxidised. This is due to the removal of the active sites that were previously introduced by the oxidation treatment. Therefore, it was confirmed that treatment at 1100ºC actually removes the active sites for the ODH, which were assigned to carbonyl/quinone group.

Santiago et al. (2005) used a commercial AC in TBR at 140ºC and 0.2 MPa of oxygen partial pressure, achieving up to 50% phenol conversion. They stated that this performance may be due to the adsorption capacity of AC, which enhances the oxidation environment conditions. After acid treatment with HNO_3, H_2O_2, $(NH_4)_2S_2O_8$ and HCl, an increase in the surface oxygen content was observed by elemental analysis, Boehm titration and thermogravimetric analysis. Specifically by Boehm titration, it was found that this acid treatment increased the total acidic sites, up to 73 % in the treatment with $(NH_4)_2S_2O_8$. This increase in the acidic functionalities by $(NH_4)_2S_2O_8$ treatment had been also seen by other researchers (Pradhan et Sandle, 1999; Heinen et al., 2000; Strelko et al., 2002). In addition, the catalytic activity of these carbons was tested in the TBR. It was clearly demonstrated that the acid treatment diminishes the catalytic performance of the carbon, down to 25 % in the case of HCl treatment, which suggest that demineralisation could play some role in this result.

Other treatments like iron impregnation have been done on AC used as catalyst specifically in the oxidation of phenol. Zazo et al. (2006) impregnated iron on a commercial AC and tested the modified carbon as catalyst in the oxidation of phenol in batch at 50ºC and promoted by H_2O_2. The added iron significantly increased the catalytic activity in presence of peroxide, reaching a 100% conversion after 120 min.

In spite of the efforts dedicated to the study of AC as catalyst, the factors that influence the catalytic activity are not well established or even determined. In any case, it has been extensively demonstrated that AC can be modified in a wide variety of ways in order to improve its performance depending on the target compound to be adsorbed or reacted, which open many possibilities to the design of tailored activated carbons for CWAO.

Chapter II

“If you do not know how to ask the right question, you discover nothing.”
William Edwards Deming, 1900-1993

Hypothesis and Objectives

2.1. Hypothesis

Every day, stronger regulations are applied to industries for the safe disposal of hazardous effluents. Nowadays, wastewater treatments should deal with very complex mixtures of compounds, and the available materials typically used in wastewater treatments as adsorbents or catalysts are not always suitable for the kind of treatment needed. As stated, oxidation in aqueous phase is one of the most popular treatments used for the elimination of refractory compounds. However, the need of expensive oxidants, such as O_3 or H_2O_2, or high value metal catalysts that in addition present leaching are drawbacks that limit the wide implementation of this technique.

AC can be successfully applied in wastewater treatments as adsorptive material (Chapter I, section 1.4.2.1), metal support (Chapter I, section 1.4.2.2) and catalyst by itself (Chapter I, section 1.4.2.3). In each case the performance of the AC depends on the chemical and physical characteristics of the material. Fortuny et al. (1998, 1999), Stüber et al. (2001), Suárez-Ojeda et al. (2005), Santiago et al. (2005) and Santos et al. (2005) have provided many evidences demonstrating that AC can successfully be used as catalyst in the catalytic wet air oxidation of phenol (CWAO) under mild conditions of pressure and temperature. However, the true role of AC in this process remains mostly uncertain. Several hypotheses could be established when considering the characteristics specifically responsible for the catalytic properties of AC in the CWAO of phenol.

The activated carbon surface could play a key role in the organic oxidation through different ways. On one hand, phenol adsorption could be one step of the oxidation mechanism. On the other hand, AC could help the formation of radicals from the dissolved oxygen. In both cases, the AC surface properties would be determinant for this performance as catalyst. Number and type of surface oxygen functionalities could be determinant for the adsorption of phenol on the surface of AC. If the availability of phenol molecules for the free radicals generated by the AC surface is considered as an important factor in the catalytic performance, the effect of phenol adsorption on carbon should be considered. Several heat treatments under inert and oxidant gas atmospheres were designed in order to modified the surface oxygen groups content in some commercial AC. Nitrogen and hydrogen were chosen for the elimination of oxygen from surface under heat treatment. Different temperatures were also used for a selective elimination of oxygen functionalities. Air was used as oxidant when some specific oxygen groups were desired on the AC surface, in order to test the catalytic behaviour of the carbon with only one kind of the different surface oxygen functionalities.

Textural properties should also be evaluated when considering possible characteristics affecting the catalytic properties of AC. Depending on the compound molecule size, it is better adsorbed on different pore size of the carbon (micro, meso and macropores). As previously stated, the adsorption could be a parameter involved in the catalytic behaviour presented by AC. Therefore, if textural properties affect the adsorption capacity, there could be also inferred to affect the catalytic behaviour shown by AC. In this case, several AC with different porosity have been tested as catalyst in the CWAO of phenol in order to assess the impact of this parameter.

The raw material used for the manufacture of activated carbon could be also critical for the chemical characteristics that this material later presents. It is known that carbons made from coal show considerable amount of inorganic material, whereas carbons made from agricultural wastes like coconut shells do not present this high mineral matter content. Considering that the ash content of AC is mainly formed by metals (Ca, Mg, Si, Fe among others) and its salts, it is possible that one or several of these metals could impart catalytic activity and be responsible of that in oxidation reactions. To evaluate the impact of the metal content, different commercial AC, made from coal, wood and coconut shells were tested as catalyst in the CWAO of phenol and its catalytic performance evaluated considering the presence of inorganic matter on the carbon. In addition, some ACs possessing catalytic activity were demineralised to check the effect on that activity.

In fact, each characteristic above mentioned or combination of them could be responsible for the actual catalytic activity show by certain carbonaceous materials in oxidation reactions.

2.2. Objectives

The main objective of this research work is the design of an experimental procedure for synthesising tailored activated carbons with suitable surface chemistry, textural properties and mineral content giving good catalytic performance in phenol wet oxidation.

To achieve this general goal, several secondary objectives can be drawn, related with the effect of different parameters on the catalytic activity of the AC. In first place, the characterization of a commercial AC, with proven catalytic activity for the phenol oxidation reaction, must be conducted. Data about elemental composition, textural properties, such as surface area and porosity, and also the surface chemistry should be related to the catalytic performance.

Then, several commercial activated carbons will be characterised in the same way and their catalytic activity compared between them. The catalytic behaviour will be tentatively related to the different characteristics of these AC.

The next step is carrying out modifications on AC in order to modify the content of surface oxygen groups. The effect of the presence of the different type of these groups in the catalytic activity of AC will be assesed by conducting three main modifications: total elimination from surface, partial or selective elimination, and finally by the creation of some specific functionalities once the carbon surface is practically free of oxygen groups.

As previously stated, the mineral content might have importance when trying to elucidate the characteristics that make AC effective as catalyst in the phenol CWAO because of the possible presence of metals with catalytic properties. In order to clarify the effect of metal content, specifically the effect of iron, one of the commercial carbons will be treated for reducing and increasing the content of this metal. Full characterisation will also be done in these modified samples. Their performance will also be tested in phenol adsorption and in phenol oxidation.

Once the best AC is identified, its chemical surface and characteristics in general will be reproduced by the design of an experimental procedure for the functionalisation or modification of any carbonaceous material, in order to obtain a tailored activated carbon from any potential carbon source, which efficiently performs as catalyst for the phenol oxidation in aqueous phase.

Chapter III

Methodology

In this chapter, a brief description of the analytical techniques used and procedures followed during the development of this research work is made.

3.1. Materials.

Several commercial activated carbons were examined. Table 3.1.1 summarises the name, the manufacturer, the origin and the label hereafter assigned to each commercial activated carbon used. Prior to use, the activated carbons were crushed and sieved with a CISA RP.08 sieve. Later, the 0.3-0.7 mm (25-50 mesh) size particle range was separated. The above fraction was repeatedly washed to remove all fines and oven-dried overnight at 105ºC. Then, it was stored in amber bottles until use.

Table 3.1.1. Commercial activated carbons used in this work.

Name	Manufacturer	Origin	Label
Merck (ref. 2514)	Merck	Coal	ME
Nuchar®WV-B	Mead Westvaco	Wood	WV1
Nuchar®RGC	Mead Westvaco	Wood	WV2
GH-6112	Warwick Benbassat	Coconut	GT
Cyclecarb 301	Chemviron Carbon	Coal	IR
Filtrasorb®400	Chemviron Carbon	Coal	F400
Centaur®HSV	Chemviron Carbon	Coal	CN
HD4000	Norit Inc. (USA)	Coal	HD

Two additional carbons derived from HD were received from the Environmental Engineering and Science Department of Clemson University (South Carolina, USA). In one case extensive washing with 1 N HCl followed by washing with deionised water was conducted. The objective of this treatment was to significantly reduce the inorganic content (including iron) of the HD carbon; this sample was labelled HDD. Secondly, HDD was heat treated under steam at 800ºC for 5 h (until reaching an approximate burn-off of 45%) for opening the pores and increasing the mesoporosity. The HDD thus treated is termed HDDS. These samples were prepared by Dr. Dastgheib of the Dr. Karanfil’s research group at the mentioned University.

Crystallized phenol for preparing feed solutions in the TBR and adsorption tests was purchased from Panreac (ref. 144852.1211, 99.9% purity). HCl and NaOH solutions used for the Boehm method were standard tritation solutions, whereas Na_2CO_3 and $NaHCO_3$ had 99.9% purity. All they were supplied by Sigma Aldrich.

Sulphuric and nitric acids, used in the acid wash pre-treatment before metal impregnation, were also supplied by Sigma Aldrich. Sodium acetate and iron chloride were used as source of calcium and iron ions needed in the modification by metal impregnation. They were also supplied by Sigma Aldrich. Deionised water (DI) was used to prepare all the solutions. Air and nitrogen was supplied by Carburos Metálicos, S.A. with over 99.995% purity.

For the manufacturing of AC with specific textural and chemical properties done in the last part of this work, two different raw materials were used: wood, specifically willow, and coconut shells, both provided by the Imperial College of London. All the raw materials were used as received. Both the coconut shells and the pieces of willow had an original average size of 2-3 cm.

3.2. Activated carbon characterisation.

3.2.1. Textural properties

As stated in the theoretical section, textural properties of activated carbon, such as surface area and porosity, are determinant in the performance of this material. In most of the cases, these parameters can be calculated from data obtained from nitrogen adsorption isotherms made at 77K. The nitrogen fills micro (pore diameter smaller than 2 nm) and mesoporous (2-50 nm). However, carbon dioxide is better used for measuring narrow microporosity (pore size diameter smaller than 0.7 nm) and enters porosity which is not available to N_2 at 77K due to kinetic restrictions. The adsorption isotherm provides a lot of information about the porosity of carbons, but this information should be interpreted in order to assign one value to the surface area or porosity volumes. The most common models used for the data treatment obtained from N_2 are the BET (Brunauer–Emmett-Teller, Eq. 2) for surface area and DR (Dubinin-Radushkevich, Eq. 3) for micropore volume. The central assumptions of the BET equation are that the adsorbent surface is homogeneous, there are no adsorbate-adsorbate interactions and it considers the possible formation of multilayers on open surfaces. The DR equation is not based on a model of adsorption process. It is a derivative of the mathematics of Rayleigh, Gaussian or Lorentzian (Marsh and Rodríguez-Reinoso, 2006). The Horwath and Kawazoe theories (Horwart et al., 1983) can be also used as alternative for the calculation of micropore volume.

$$\frac{p}{V*(p^0-p)}=\frac{1}{V_m*c}+\frac{c-1}{V_m*c}*\frac{p}{p^0} \qquad \text{Eq. 2}$$

$$W=W_0*\exp\left[-RT/\beta*\log^2(p^0/p)\right] \qquad \text{Eq. 3}$$

p: equilibrium vapour pressure
p^0: saturation pressure

V: amount adsorbed in volume at STP
V_m: monolayer capacity in volume at STP
c: BET parameter indicative of the energetics of the adsorption process
W: volume of adsorbate filling micropores
W_0: total volume of the micropore system
β: affinity factor

Mesoporosity has also been studied from different calculation methods. Most of them assume that the pore surface condensates the adsorbate in a continuous way until is filled, but without any phase change occurring spontaneously. The only difference between them is the mathematical approximations made to solve the analytical numerical calculations. From these methods the most important is the BJH, from Barret-Joyner-Halenda, (Barret et al., 1951).

The characterisation of the porous texture of the activated carbons used in this study was done using physisorption of N_2 and CO_2 at 77 and 273 K respectively. Nitrogen adsorption was used for determining the total volume of micropores whereas the adsorption of CO_2 at 273 K allowed to asses the narrowest micropores. Before adsorption, 100 mg of each sample were degasified under vacuum for 24 hours at 200ºC in order to remove impurities initially adsorbed on AC surface. For the calculation of the surface area, the BET model was used. However, whereas for the calculation of microporosity volume values, the DR equation was preferred, as it is valid even in a very low relative pressure range. Total pore volume was calculated from the near saturation uptake, i.e. at the relative pressure of 0.98.

Since some parts of this work were done in collaboration with other universities, different equipments were used for the N_2 adsorption/desorption isotherms. The analysis performed in the University of Alicante was done in an Autosorb-6 apparatus. Analyses done in the Universitat Rovira i Virgili were made using a Micromeritics 2020ASAP instrument. All the samples modified by iron and calcium impregnation made in collaboration with the Ecole des Mines of Nantes were analysed in a Micromeritics 2010ASAP instrument and mesopore and micropore volume were estimated according to BJH and HK theories respectively. The degasification in this case was done at 250ºC.

3.2.2. Thermogravimetric analysis

Thermogravimetric analyses (TGA) were give the weight change under heat treatment and allows assessing of the amount of the adsorbed species. Samples (about 20 mg) were heated from 100 to 900ºC under nitrogen flow at a heating rate of 10ºC/min in a Perkin-Elmer Thermobalance, model TGA7.

3.2.3. Temperature Programmed Desorption.

The characterisation of the oxygen surface groups present in AC was conducted by temperature programmed desorption (TPD). This technique only was applied over samples analysed in the University of Alicante, since it was not available at the other places. During the thermal decomposition of the surface groups, carboxylic, lactones and anhydrides evolve in CO_2, while CO is mainly a decomposition product of quinones, hydroquinones and phenols (Boehm, 2002). The experimental system for TPD experiments consisted of a thermobalance SDT TA Instruments 2960 coupled to a mass spectrometer Balzers MSC 200 Thermostar. Helium was used as carrier and the heating rate was 20ºC/min, from room temperature up to 950ºC. CO and CO_2 were detected with a GC-MS system. The quantification of CO and CO_2 was done by comparing the signal obtained with that of several calcium oxalate monohydrate calibrations done in the system.

3.2.4. Boehm titrations.

Boehm method (Boehm, 2002) was used to determine the acidic surface functional group content of the AC's. Solutions of $NaHCO_3$, Na_2CO_3 and NaOH (0.05 N) were prepared using DI water. 25 cm^3 of the base solution were added to 1 g of carbon in a 30 ml glass flask. Then, they were allowed to equilibrate for one day at room temperature without agitation. At the end of the equilibration period, the carbon was separated from the solution by filtration, and the filtrate was titrated using standardised HCl solution in an automatic titrator CRISON Titromatic 2S. The number and type of acidic sites were calculated by considering that NaOH neutralises carboxylic, lactonic and phenolic groups, that Na_2CO_3 neutralises carboxylic and lactonic groups, and that $NaHCO_3$ neutralises only carboxylic groups. Carboxylic groups were therefore quantified by direct titration with $NaHCO_3$. The difference between the groups titrated with Na_2CO_3 and those titrated with $NaHCO_3$ was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na_2CO_3 was assumed to be phenols. Each determination was performed by duplicate.

3.2.5. pH at the point of zero charge.

The mass titration method (adapted from Noh and Schwarz, 1989, and Menéndez et al., 1996) was used to determine the pH at the point of zero charge (pH_{pzc}) of each sample. To determine the right concentration of carbon, a titration curve was first obtained. Different carbon concentration slurries in deionised water were prepared, then shaken for 24 h and the final pH of the slurry was measured with the pHmeter described in section 3.3.3. For values greater than 5% wt the pH value obtained was constant. Therefore, for all samples, this amount of carbon was used and the resulting pH taken as the pH_{pzc}.

3.2.6. Metal content.

In order to determine the metals present in AC samples, 50 mg of carbon were digested in 2 ml of concentrated nitric acid in a microwave digestion equipment PAAR, model M627. Dilute solutions (2:50 acidified with 1% of nitric acid) were analysed by Inductively Coupled Plasma (ICP) atomic emission in a Perkin Elmer Plasma 400 Emission Espectometer. With this dilution factor, the amount of metal in solution was in the range of the calibration curve done for each metal, 0-2 ppm. However, for specific measure of iron or calcium content, atomic absorption spectrophotometry (AAS) was used following the same procedure above described with a Hitachi Z-8200 Polarised Zeeman spectrophotometer.

3.3. Characterisation of the liquid solutions.

3.3.1. HPLC & GC

For measuring the concentration of the phenol and the rest of organic species identified as intermediate products of phenol oxidation, High Pressure Liquid Chromatography (HPLC) was used. First, a selection of the main and more representative intermediates compounds found in the liquid sample after phenol oxidation was done. This selection was done according to the oxidation pathways generically proposed in the literature (Devlin et al., 1984; Joglekar et al., 1991) and in previous results reported by Suárez-Ojeda (2006). The HPLC used was an Agilent Technologies 1100 Series, with a C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm). For measuring phenol concentration, the mobile phase was a 35:65 % v/v mixture of methanol and deionised water, acidified at pH equals to 1.41 with H_2SO_4, at a flow rate of 1 ml/min. The detection of phenol was performed by means of UV absorbance at a wavelength of 254 nm. A different protocol was developed using solvent flow gradient for measuring the concentration of partial oxidation products from the phenol. The gradient started from 100% of water and progressively changes to 50:50 %v/v in 25 minutes, keeping this end mobile phase concentration until minute 37. The flow rate was 0.75 ml/min and the wavelengths used in the diode array detector (DAD) were 210 and 254 nm, depending on the compound . Table 3.3.1 lists some intermediates identified and measured in the liquid samples from TBR tests in order of appearance during the analysis.

Figures 3.3.1 and 3.3.2 are two examples of typical chromatograms taken from the reports obtained after HPLC analysis. The main intermediate compounds are identified and its concentration reported according to a previous calibration done.

In some cases phenol concentration from the adsorption isotherms was measured by GC in a GC6890 (Agilent technologies). A HP-5 (5% phenyl-methyl-solixane, 30 m x 0.32 mm i.d. x 0.25 µm film thickness) capillary column was used with a temperature program starting at 40ºC for 6.30 min, then raising up the temperature to 60ºC (at 20ºC/min) and finally a second raise from 60ºC to 120ºC (at 30ºC/min). The injection volume was 0.5 µm and the injector temperature was 250ºC. The carrier gas was helium (99.99% pure, 13.5 ml/min) and phenol was detected using a flame ionisation detector (FID) at 300ºC. Results from GC were comparable to those obtain from HPLC, however, not all the oxidation intermediates can be measured by GC, so that it was applied only when phenol was wanted to be measured.

3.3.2. Total organic carbon.

The Total Organic Carbon (TOC) is another mean for measuring the organic matter present in wastewater. This test is performed by injecting a known quantity of sample into a high temperature furnace in a chemically oxidizing environment. Thus the organic carbon is oxidised to carbon dioxide in the presence of a platinum catalyst (Tchobanoglous and Burton, 1991). In samples from TBR, the TOC was measured in a TC Multi Analyser 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector. Sample acidification and aeration prior to analysis eliminate errors due to the presence of inorganic carbon.

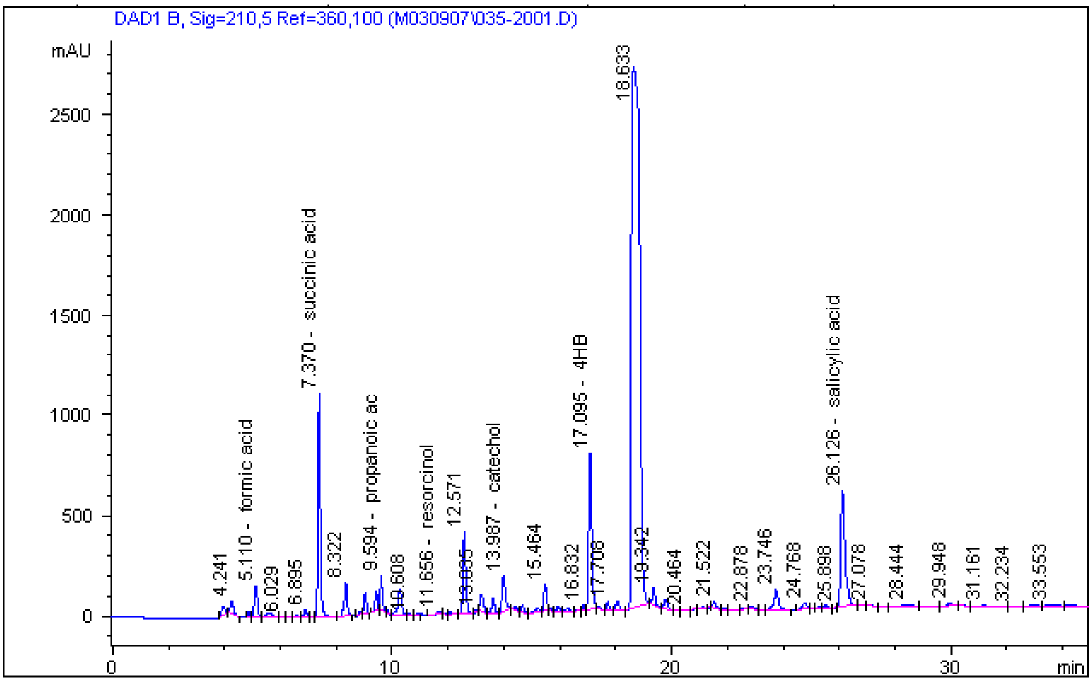


Figure 3.3.1. Chromatogram from HPLC report with intermediate compounds measured at UV wavelength of 210 nm.

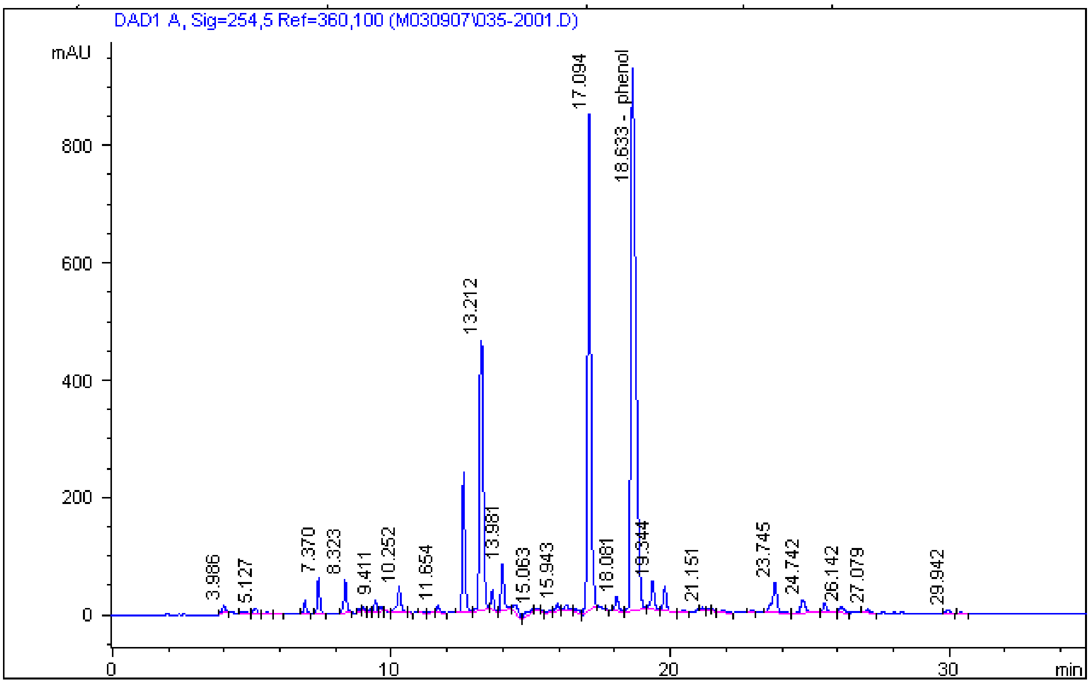
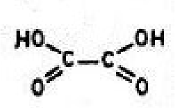
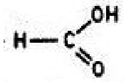
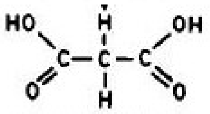
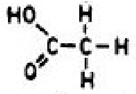
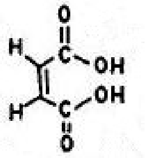
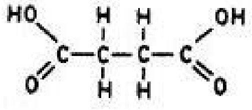
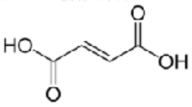
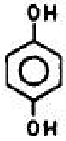
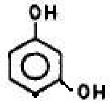
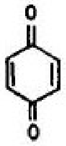
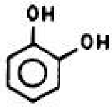
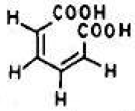
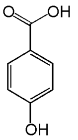
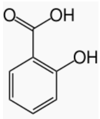


Figure 3.3.2. Chromatogram from HPLC report with intermediate compounds measured at UV wavelength of 254 nm.

Table 3.3.1. Intermediates identified and measured in the liquid samples from TBR.

Type of compound	Compound	Chemical structure	Retention time (min)	Wavelength (nm)
Linear chain	Oxalic acid ($C_2H_2O_4$)		3.228	210
	Formic acid (CH_2O_2)		3.568	210
	Malonic acid ($C_3H_4O_4$)		4.540	210
	Acetic acid ($C_2H_4O_2$)		5.034	210
	Maleic acid ($C_4H_4O_4$)		5.947	210
	Succinic acid ($C_4H_6O_4$)		7.096	210
	Fumaric acid ($C_4H_4O_4$)		7.611	210
Aromatic	Hydroquinone ($C_6H_6O_2$)		8.526	254
	Resorcinol ($C_6H_6O_2$)		11.493	254
	p-Benzoquinone ($C_6H_4O_2$)		12.360	254
	Catechol ($C_6H_6O_2$)		13.151	254
Linear chain	t,t-Muconic acid ($C_6H_6O_4$)		14.493	210
Aromatic	4-Hydroxibenzoic acid ($C_7H_6O_3$)		17.094	210
	Salicylic acid ($C_7H_6O_3$)		27.683	210

3.3.3. pH

The pH was directly measured over the liquid samples using a pHmeter model CRISON GL21 equipped with an K/KCl electrode.

3.4. Modification of the activated carbon.

3.4.1. Thermal treatment.

Thermal modifications were performed using a quartz tube reactor placed inside a temperature-controlled oven. Temperature was controlled with a FUJI PX V4 controller, with an accuracy of ±1ºC. For all thermal treatments, 15 g of AC were load into the reactor. When conducted under controlled atmosphere either of nitrogen, hydrogen or air, a 50 cm^3/min (STP) gas flow rate was used. Figure 3.4.1 schematically depicts the equipment used for the thermal gas treatment.

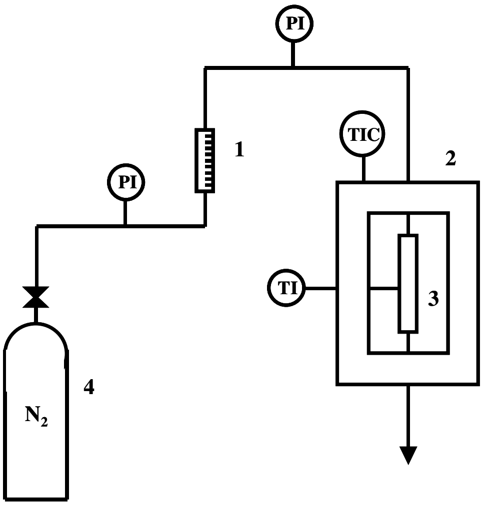


Figure 3.4.1. Experimental set-up for AC modifications: (1) Gas flowmeter, (2) Oven (3) Glass reactor and (4) Gas cylinder.

For thermal treatment under nitrogen, any sample was first heated at a rate of 20ºC/min from 20ºC to 100ºC, keeping the sample at this temperature for 10 min in order to remove the moisture. Then, three different samples were prepared by heating until three different temperatures -400, 700, and 900°C- with a heating rate of 10ºC/min. Then, the samples were kept at the final temperature for 105 min. After the treatment, the carbons were cooled under nitrogen. These samples are referred to as ME400, ME700 and ME900 respectively, since only ME was used in this part of the research.

For thermal treatment under hydrogen, the sample was first warmed up under nitrogen from room temperature up to 100ºC at 10ºC/min, kept at this temperature for 15 min, then heated until 900ºC with a heating rate of 20ºC/min. When 900ºC were reached, nitrogen was switched to hydrogen, and the temperature maintained for 3 h. Finally, the sample was cooled under nitrogen to room temperature. AC's thus obtained are denoted

by their name followed by –H. These procedures were adapted form previous studies of Dastgheib et al. (2004) for instance.
In order to evaluate the effect of some specific AC surface oxygen functionalities, an experimental procedure was designed using combinations of N_2, H_2 and air. Nitrogen was used for the elimination of acidic functionalities from surface, hydrogen was used to stabilise the active sites remaining in the surface avoiding its further oxidation, whilst air was used as oxidant to create lactonic and phenolic functionalities.

For the gas phase oxidation of AC, the following procedure was designed:

- First the sample was heated under nitrogen with a heating rate of 10ºC/min from 20ºC to 100ºC, keeping the sample at this temperature for 15 min in order to eliminate moisture. Then, it was heated until 900°C at a heating rate of 20ºC/min and keeping the final temperature for 3 hours.
- Then, the sample was cooled in N_2 until 400ºC.
- Next, oxidation with a mixture of 8% O_2 in N_2 was conducted at 400ºC for 2 hours.
- After the oxidation, the sample was heated under N_2 up to 600ºC and kept at this temperature for 1 hour.
- Then, the sample was cooled to 50ºC under N_2 and then treated under H_2 at this temperature for 1 hour.
- Finally, samples were cooled to room temperature under N_2.

The mixture 8% of O_2 in N_2 was done considering that the air supplied by Carburos Metálicos is a mixture of 79% nitrogen-21% oxygen, so the flow of the two gases were adjusted to obtained the desired oxygen concentration.

3.4.2. Acid treatment.

Some carbons were partially demineralised in 1 L of 0.1 N HCl solution stirred for 24 hours. The mass concentration was 4%wt of AC. The HCl solution was then replaced with fresh acid solution to maintain the initial conditions and stirred for another 24 hours. Those carbons are labelled as the AC name followed by D.

Nitric acid wash was conducted in two ways. Carbons treated in the URV were boiled in an excess of this nitric acid with a concentration of 4% wt, for 1 hour. Exited vapours were bubbled in water. Samples were later thoroughly washed with water until neutrality, and dried overnight at 105ºC. The treatment is denoted as N1 in the samples.

In the Ecole des Mines of Nantes, the acid wash was made as a pretreatment for the metal impregnation in a rotavapour at 80ºC. The HNO_3 was 65% v/v and 170 ml of HNO_3 were mixed with 35 g of ME. AC was in contact with acid for 3 hours. Then, it was washed with DI water until neutral pH and dried overnight at 105ºC. This treatment is hereafter referred to as N.

For sulphuric acid wash, a carbon sample was boiled for 1 hour in 96% H_2SO_4. The weight to weight ratio of acid to dried AC was 9:1. Then, it was washed with DI water until neutral pH and dried overnight at 105ºC. This treatment is indicated by a S following the name of the AC.

3.4.3. Metal Impregnation.

Iron impregnation was performed by the ion-exchange method. AC samples were immersed for two days in a $FeCl_2$ solution at 2% wt Fe concentration in an orbital shaker. This impregnation was conducted on ME, MEN and MES. Calcium impregnation was performed by the same method but using calcium acetate, $Ca(CH_3COO)_2$, at 0.4% wt Ca concentration. This experimental procedure was adapted from the work made by Lorenc-Grabowska et al. (2004). Since the objective of the calcium is to enlarge the porosity with the subsequent gasification, the concentration used of this metal was lower than the concentration of iron. This impregnation was also conducted on ME, MEN and MES. Carbon ME was also impregnated with the two metals. The procedure was the same either for Ca and Fe, but the calcium impregnation was done first and later that with iron. At the end of these treatments, all the samples were recovered, washed with DI water until neutral pH, and dried overnight at 105ºC. All metal impregnated AC's were subsequently carbonised in an 2 L horizontal furnace under nitrogen atmosphere at a heating rate of 20ºC/min up to 1000ºC and then let to freely cool until room temperature under nitrogen flow. The iron impregnated AC's are labelled correspondingly as MEFe, MENFe and MESFe. Correspondingly, the calcium impregnated carbons are labelled as MECa, MENCa and MESCa. The carbons impregnated with both metals were labelled MECaFe, MENCaFe and MESCaFe.

3.5. Tailored AC manufacturing.

Activated carbons prepared in the Imperial College of London were made on a modified Carbolite HTR 11/150 laboratory-scale rotary furnace. The raw material was heated at 10ºC/min to different temperatures under a flowing nitrogen atmosphere (500 ml/min).

For samples made from wood (willow) by one-step pyrolysis and activation with steam, a final temperature of 800ºC was fixed. Once this temperature was reached, the inert atmosphere was replaced by a mixture of steam/nitrogen by injecting distilled water by means of a calibrated peristaltic pump, which was set to work at a constant flow of 0.812 ml/min. These conditions were kept for 1 hour and then the steam flow stopped and the carbon cooled under nitrogen. Samples thus obtained are referred to as MW1.

For the AC made from wood by chemical activation, KOH was selected as activation agent and a direct impregnation of the raw material was performed. The mass ratio was 3:1 KOH:wood. The final temperature for the activation was 750ºC and it was kept for 1 hour. This carbon was also made in one single step and no steam was used in this case. The heating rate and nitrogen flow have the same value indicated before, 10ºC/min and 500 ml/min.

The AC made from wood with high iron content was prepared by impregnation of 160 g of raw material with a $FeCl_2{\cdot}4H_2O$ 0.1 M solution for 24 hours. The willow concentration was 6% wt. After 24 hours in contact with the iron solution, willow was filtered and dried overnight at 105ºC. The willow was then impregnated with KOH at the same conditions already explained for chemical activation and heated up to 500ºC under nitrogen atmosphere (500 ml/min).

For the preparation of AC from coconut shells, the same one-step pyrolysis/activation with steam described above was conducted. In this case, based in the results collected in the review made by Ioannidou and Zabaniotou (2007) and the intention of obtaining a microporous material, a higher temperature was selected for the activation. Thus, the activation was done at 1000ºC and the water flow was 0.813 ml/min.

The AC made from coconut shells with high iron content was prepared in two steps. First, the raw material was heated under nitrogen up to 450ºC in order to produce a char free from volatile species and condensable oils. This char was then impregnated with a $FeCl_2 \cdot 4H_2O$ 0.1 M solution for 24 hours, and then filtered and dried overnight at 105ºC. Once moisture free, it was then heated up to 1000ºC in the oven and kept at this temperature for 1 hour under a mixture of steam/nitrogen as previously described. Finally, the water flow was stopped and the AC was cooled under just nitrogen.

3.6. Performance tests.

3.6.1. Adsorption.

Phenol adsorption isotherms were obtained at 20ºC (±2ºC) in oxic conditions. Solutions with phenol concentrations ranging from 0.5 to 7 g/L were used to evaluate the adsorption capacity at high concentrations. An AC mass of 0.25 g was allowed, under stirring, to equilibrate with 50 ml of phenol solution at the different concentrations. Based on the work of Suárez-Ojeta et al. (2005) and Santiago et al. (2005) the equilibration time for the adsorption isotherms was set at 2 and 4 hours to evaluate the time needed to reach the equilibrium, although the results demonstrated that just 2 hours were enough to reach saturation of AC. Thus, the carbon samples were in all cases stirred for approximately 2 hours in the phenol solution, and left 0.5 hour to let the AC to settle. An aliquot of 2 ml was then filtered, and the final concentration of samples was determined by HPLC as explained in subsection 3.3.4.

3.6.2. Trickle bed reactor operations.

CWAO experiments were carried out in a trickle bed reactor in downflow co-current. The scheme of the experimental set-up is shown in Figure 3.6.1. 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. A detailed scheme of the reactor is shown in Figure 3.6.2, which corresponds to the element 5 in the Figure 3.6.1. The air flow rate was measured and held constant with a gas flowmeter coupled with a high precision valve at 2.4 STP cm^3/s. The liquid weight hourly space velocity was set to 8.2 h^{-1}, which is equivalent to a space time of 0.12 h. Thus, the appropriate liquid flow rate was fixed according to the weight of the catalytic bed. The liquid flow was stabilised with a pulse dampener and measured with an automatic liquid flowmeter (Iberfluid Technical, Spain). This value was selected based on the work made by Stüber et al. (2001) in order to assure working in trickle regime and since it gives approximately 40% conversion with ME at the selected pressure and temperature, which allows for performance comparison with other ACs. Phenol feed concentration was always 5 g/L. The liquid feed was stored in a 5 L stirred glass tank and it was pumped by a high precision metering pump (Eldex, Recipro HP Series model AA-100-S-2 CE) that could deliver up to 500 ml/h at a maximum pressure of 350 bar. At the exit of the reactor, the products of the reaction were rapidly cooled, before separating the liquid and gas phases. This separation was carried out in two vessels, the smallest one being used for taking liquid samples that were periodically withdrawn. The experimental conditions were fixed at a temperature of 140ºC and 2 bar of oxygen partial pressure to ensure an excess over the stoichiometric oxygen uptake needed. The experiments were run for 55 hours. Liquid samples were then analysed to determine phenol conversion (X) and TOC abatement (X_{TOC}). Also pH was measured in all the samples.

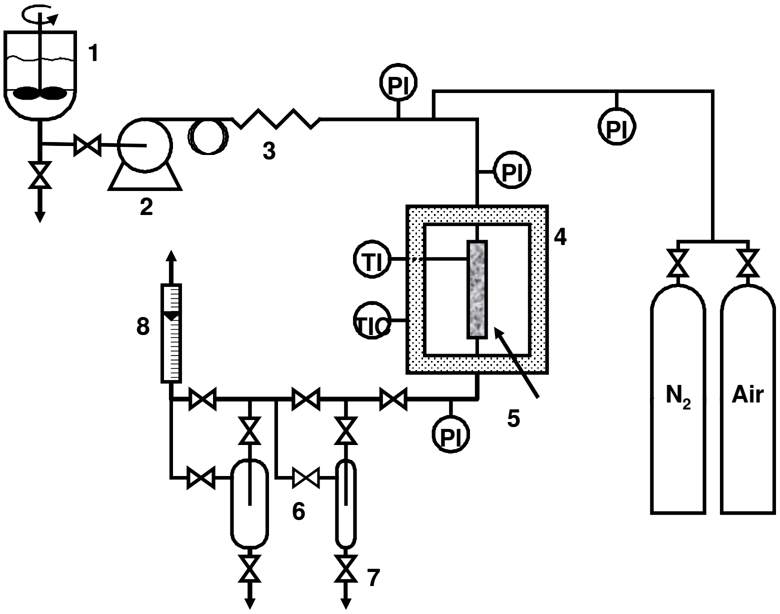


Figure 3.6.1. Experimental Set-up for the CWAO: (1) Feed, (2) High pressure liquid pump, (3) Pulse dampener and liquid flowmeter , (4) Oven, (5) Reactor, (6) Separators, (7) Sampling and (8) Gas flowmeter.

Performance of the different materials tested was done in terms of phenol conversion, X, and TOC abatement X_{TOC}. Both were calculated using the following general expression:

$$X(\%) = \frac{C_o - C_e}{C_o} x100 \qquad \text{Eq. 4}$$

where C_o is the inlet concentration of either phenol or TOC and C_e the corresponding concentration in the exited effluent.

A list of all the activated carbons, either commercial, modified or home-made tailored, tested for CWAO of phenol in the trickle bed reactor is given in Table 3.6.1.

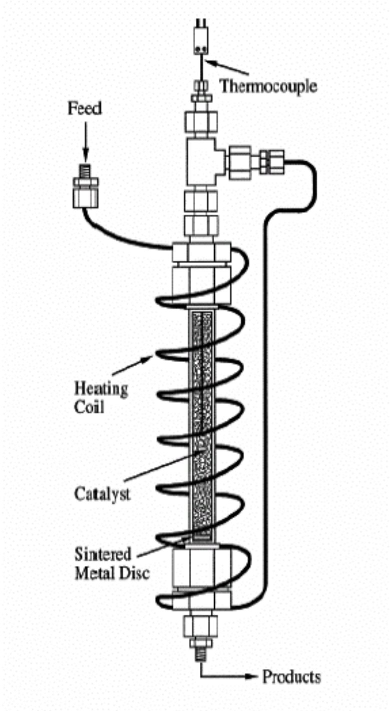


Figure 3.6.2. Detailed scheme of the fixed bed reactor.

3.6.3 Trickle essays with homogeneous iron.

In order to assess the catalytic effect of homogeneous iron in the liquid phase, two essays were performed adding iron sulphate in the feed solution at a concentration of 20 mg/L of iron. In one case, the reactor was filled with activated carbon ME. In the other case, it was loaded with silicon carbide, also known as carborundum, which is an inert material. Both experiments were performed as described in the previous section, at the same conditions of temperature and pressure and also for 55 hours.

Table 3.6.1. List of all the activated carbons tested in this study.

Sample	**Modification**
ME	Original
ME400	Heat treatment under N_2 up to 400ºC
ME700	Heat treatment under N_2 up to 700ºC
ME900	Heat treatment under N_2 up to 900ºC
MEH	Heat treatment under H_2
MEO	Heat treatment under N_2 + H_2 + Air
MEN	Treatment with HNO_3
MES	Treatment with H_2SO_4
MED	Treatment with HCl
MEDH	Treatment with HCl + Heat treatment under H_2
MECa	Calcium impregnation
MENCa	Treatment with HNO_3 + Calcium impregnation
MESCa	Treatment with H_2SO_4 + Calcium impregnation
MEFe	Iron impregnation
MENFe	Treatment with HNO_3 + Iron impregnation
MESFe	Treatment with H_2SO_4 + Iron impregnation
MECaFe	Calcium + Iron impregnation
MENCaFe	Treatment with HNO_3 + Calcium + Iron impregnation
MESCaFe	Treatment with H_2SO_4 + Calcium + Iron impregnation
GT	Original
GTN	Treatment with HNO_3
GTNFe	Treatment with HNO_3 + Iron impregnation
F400	Original
IR	Original
CN	Original
HD	Original
HDD	Demineralisation treatment
HDDS	Steam treatment
HDDH	Heat treatment under H_2
HDDSH	Heat treatment under H_2
WV1	Original
WV1H	Heat treatment under H_2
WV2	Original
WV2H	Heat treatment under H_2
MW1	Physically activated – Raw material: willow
MW2	Chemically activated – Raw material: willow
MW2Fe	Chemically activated + Iron impregnation – Raw material: willow
MCS	Physically activated – Raw material: coconut shells
MCSFe	Physically activated + Iron impregnation – Raw material: coconut shells

Chapter IV

> "Nothing shocks me. I am a scientist"
> ***Indiana Jones and the Temple of Doom, 1984***

Results and discussion

4.1 Thermal treatment

In this section are presented and discussed the characterisation and performance results in phenol adsorption and catalytic activity from thermally AC treated samples.

4.1.1. Thermal treatment on carbon ME

4.1.1.1. Physical and chemical characterisation

Surface area and pore volume values presented in Table 4.1.1 indicate that ME is predominantly a microporous carbon, having about 78% of its total pore volume in the micropore region. Overall, the thermal treatment under the inert atmosphere at different temperatures did not considerably change the textural properties of the parent activated carbon. This was imperative in order to discuss the performance of these modified carbons, considering only differences in their surface chemistry. For ME that was thermal treated under hydrogen, some increase in the meso and macropore volume was observed while micropore volume and total surface area were not significantly changed. The increase in the meso and macropore volumes can be explained by the pore enlargement due to the gasification of the carbon surface by reacting with hydrogen.

Table 4.1.1. Physical properties of parent and modified AC.

Sample	**SA_{BET} (m^2/g)**	**V_{mic} (cm^3/g)**	**$V_{mes+mac}$ (cm^3/g)**	**V_{tot} (cm^3/g)**
ME	1261	0.473	0.137	0.610
ME400	1225	0.487	0.136	0.623
ME700	1262	0.514	0.128	0.642
ME900	1185	0.468	0.131	0.599
MEH	1213	0.451	0.195	0.646
MEO	n.m.	n.m.	n.m.	n.m.

n.m. Not measured

Figure 4.1.1 shows the N_2 adsorption isotherms at 77 K of the commercial ME. The shape of the isotherm fits clearly in the Type I according to the IUPAC classification of adsorption isotherms shapes. Type I isotherms reach a maximum value of adsorption without inflections and are characteristics of carbon containing only microporosity

(Marsh and Rodríguez-Reinoso, 2006). The slight hysteresis loop between the adsorption and desorption in the isotherm indicates that the mesopore volume in this carbon is considerably low.

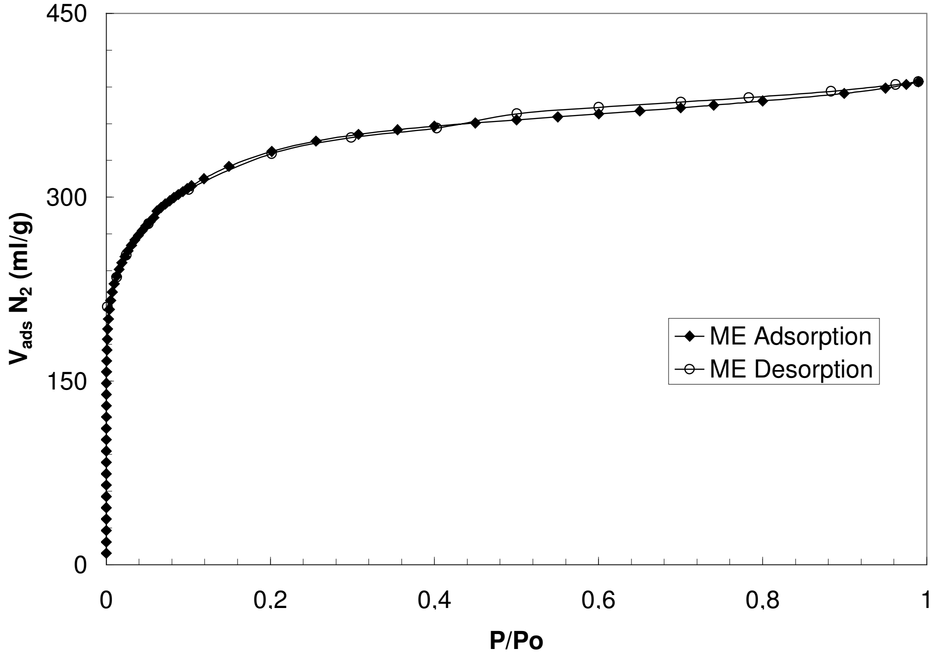


Figure 4.1.1. N_2 adsorption isotherm of carbon ME.

SEM pictures corroborate the suggestion that the carbon texture remain unaffected after thermal treatment. Figure 4.1.2 shows SEM micrographs for the original and treated ME's. These micrographs show that ME and all the treated samples have the same appearance, supporting the hypothesis that thermal treatment actually does not change textural properties of the AC, as apparently no destruction of the carbonaceous matrix can be observed.

The objective of the thermal treatment under nitrogen at different temperatures was the removal of different oxygen-containing surface groups and the production of carbons with different surface chemistry. It has been reported that most of the oxygen surface functionalities can be decomposed at 900°C, while at 400°C mainly carboxyls are removed, whereas at 700°C all the oxygen functionalities except carbonyls and quinones are expected to be eliminated from the activated carbon surface (Figueiredo et al., 1999).

The different CO and CO_2 evolving groups are indicated in Figures 4.1.3 and 4.1.4 according to the temperature range of their decomposition. It must be noted that, during heating, some parallel reactions could take place in the AC surface. Some researchers have pointed out that two adjacent carboxyl groups may be first dehydroxylated to the cyclic anhydride which, in turn, decomposes to CO and CO_2 (Boehm, 2002). This decomposition occurs at higher temperature than that of free carboxyl groups. The degradation of lactols probably will also produce both CO and CO_2. A cyclic lactone can give either one molecule of CO or CO_2 (see Figure 4.1.5).

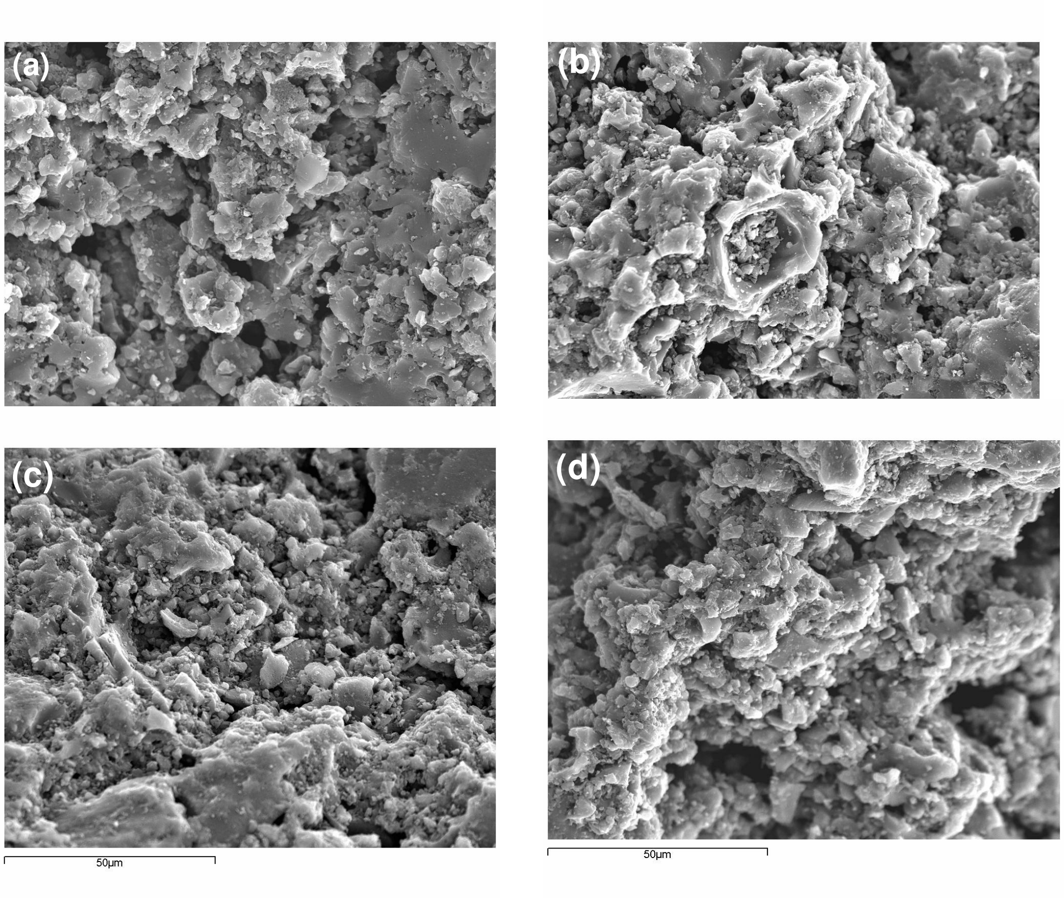


Figure 4.1.2. SEM micrographs of thermally treated samples.
(a) ME, (b) ME400, (c) ME700 and (d) ME900.

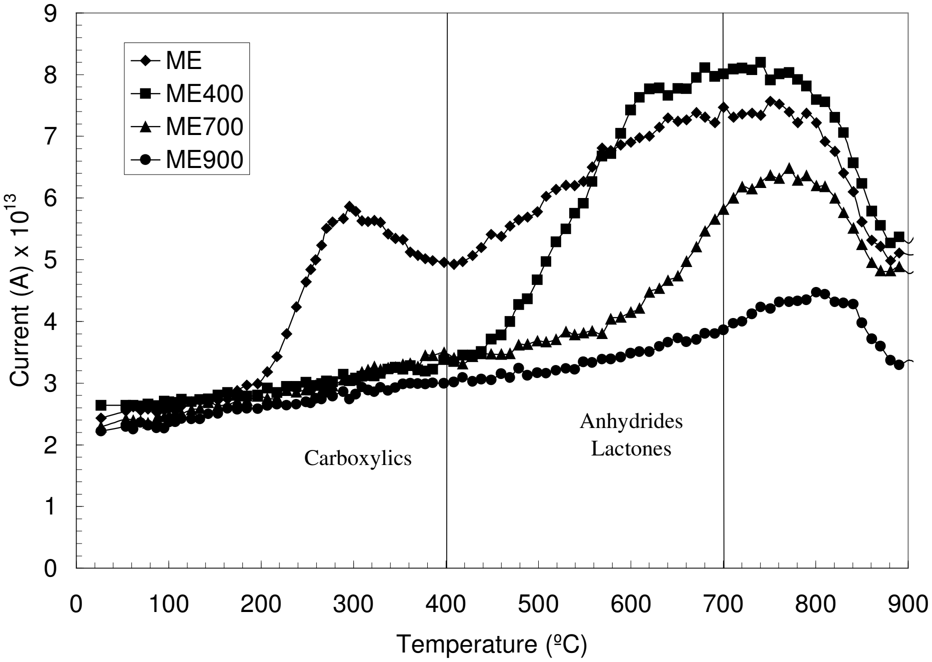


Figure 4.1.3. Signals from mass spectrometer CO_2 released.

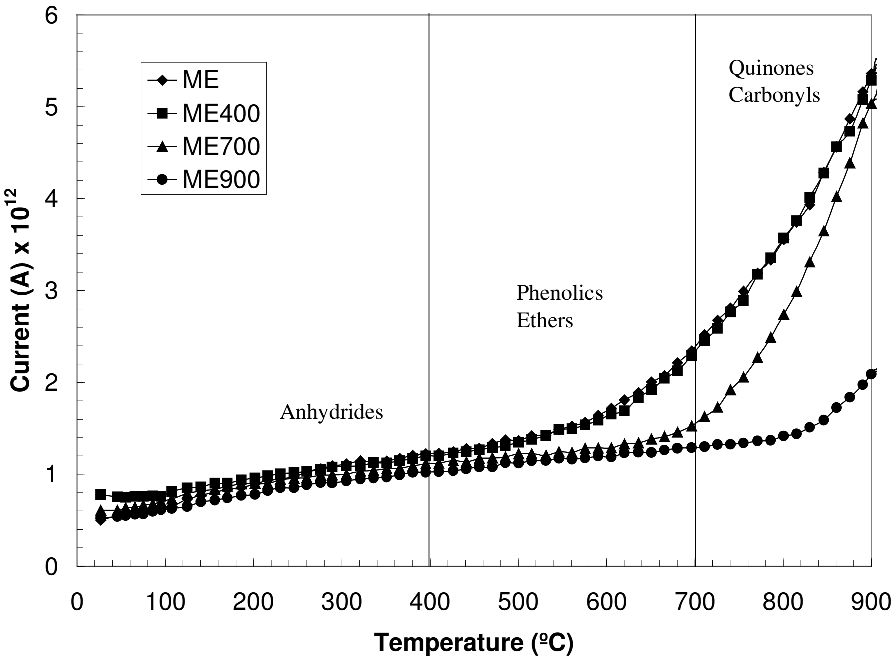


Figure 4.1.4. Signals from mass spectrometer CO released.

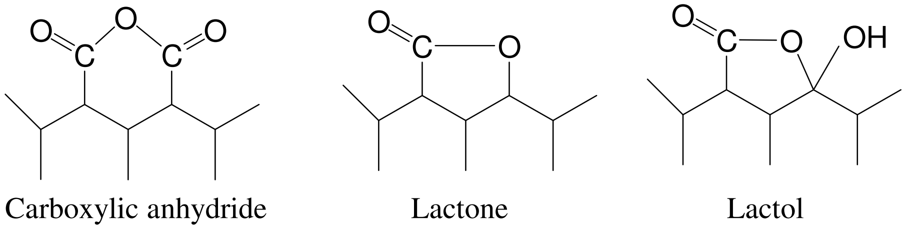


Figure 4.1.5. Possible products of condensation of surface oxygenated groups.

Also, diffusion of the evolved gases is rather slow in narrow pores. Thus, CO molecules may react to CO_2 with surface oxygen, or CO_2 molecules hitting the pore walls may form two CO molecules (Boehm, 2002). Therefore, the decomposition temperatures must actually be taken as a rough approaching to reality.

Figure 4.1.3 shows that the signal of CO_2 assigned to carboxylic groups vanishes in the samples ME400, ME700 and ME900. This proves that carboxylic groups are easily removed below 400ºC. In addition, a slight increase in CO_2 released from sample ME400 compared with ME is observed in the range from 400ºC to 700ºC. This zone corresponds to anhydrides and lactones decomposition. The occurrence of anhydrides or lactones could be attributed to the condensation of carboxylic groups. Instead, samples ME700 and ME900 show CO_2 release only above 700ºC.

An inspection of Figure 4.1.4 indicates that ME700 and ME900 also show an important decrease in phenolic and ether groups, which decomposed at temperatures higher than 700ºC in TPD. The release of CO for ME and ME400 samples are similar during TPD. This indicates that treatment at 400ºC is not capable of removing phenolics, ethers, quinones and carbonyl groups. Finally, it must be noticed that ME900 only shows significant release of CO and CO_2 beyond 800ºC. This demonstrates that most of oxygen functional groups were efficiently removed when ME was heated at 900ºC during the thermal treatment under nitrogen.

Boehm titrations support the interpretations arising from TPD's. In Table 4.1.2, the specific content of surface oxygen functional groups for all the samples are reported according to Boehm technique. In general terms, the increase in the treatment temperature produces a decrease in the carboxylic group content in all the treated samples. However, an increase of lactones is correspondingly observed for ME400. This could be due to the condensation of phenolic groups with surface carboxylic groups, favoured for the high temperature, which was already proposed by other researchers (Tessmer et al, 1997; Santiago et al, 2005; Moreno-Castilla et al, 2000; Moreno-Castilla et al, 1998). This could also explain that ME400 shows lower amount of phenolic groups than ME700. The 400ºC treatment temperature would favour the condensation reaction instead of the decomposition of this kind of groups. Also the possible formation of anhydrides by dehydration from two adjacent carboxyl groups during heating treatment has been proposed (Moreno-Castilla et al, 1998). Considering that these anhydrides can later react with adjacent phenolic groups, the increase of practically two times the content of lactones between ME and ME400 can be explained. This agrees with the CO_2 release observed in the TPD's, as discussed above, where the release of CO_2 is higher for ME400 than for original ME beyond 600ºC. This would confirm the formation of lactone groups at the thermal treatment at 400ºC.

Table 4.1.2. Chemical characteristics of activated carbons.

Sample	**Phenolics (meq/g)**	**Lactones (meq/g)**	**Carboxyls (meq/g)**	**pH_{pzc}**
ME	0.097	0.123	0.031	7.36
ME400	0.031	0.220	0.018	7.44
ME700	0.039	0.092	0.008	7.70
ME900	0.011	0.039	0.005	8.10
MEH	0.002	0.000	0.000	10.74
MEO	0.094	0.022	0.000	9.66

Moreno-Castilla et al. (1998) also proposed that, if during the thermal treatment some carboxylic anhydride groups were formed by dehydration from two adjacent carboxyl groups, these anhydrides could be rehydrated and would appear again. The presence of a small amount of oxygen groups in ME900 (see Figure 4.1.4 and Table 4.1.2) is demonstrated by the appearance of CO_2 and CO at 900ºC. Some researchers have proposed that carbonyl groups may continue evolving as CO_2 and CO from carbons heated even at higher temperature, 950ºC (Vidic et al., 1997; Papirer et al., 1991). As the treatment made reached just 900ºC, the presence of oxygen surface functional groups and their decomposition in CO and CO_2 is explained.

It has been pointed out that the acidic functional group determination by the base neutralization method account for only about 50% of the total oxygen content of the carbon and that the remaining oxygen content may be in the form of ether type oxygen, less reactive carbonyl groups or combined with mineral matter (Tessmer et al., 1997; Boehm, 2002).

During the neutralisation of HCl with NaOH when calculating the number of basic surface functional groups, the presence of mineral matter was evidenced. Samples probably have metals that leached out the carbon after being in contact with HCl. This resulted in the formation of a visible precipitate during titration of HCl filtrates from ME900. The rest of the HCl filtrates did not present the formation of visible precipitate but during neutralisation, they do change from transparent to a dark yellow colour that also evidenced the presence of mineral matter. Thus, by adding NaOH for neutralising the filtrate, the formation of hydroxides with metals does occur, causing an increase in the amount of NaOH required to reach the titration end point. Therefore, the NaOH uptake is higher that the actual amount necessary to calculate the basic surface sites, so that the quantification of basic sites is not reported. The metals present in ME were measured by ICP and will be presented later on.

The amount of CO_2 and CO released by TPD and the CO/CO_2 ratio is summarised in Table 4.1.3. The decrease in the oxygen surface groups with temperature is evident again. The decrease of oxygen groups that decomposed into CO is more gradual than the decrease of groups evolving into CO_2. In the case of CO_2 evolving groups, only above 700ºC their number decreases considerably. The values of CO/CO_2 ratio show that the maximum value is reached with the treatment at 700ºC, i.e. sample ME700. This also is proved by Figure 4.1.6, which shows the weight loss during the thermogravimetric analyses (TGA) in the parent and the thermal treated samples. Until 600ºC, the slope of all curves is smooth and most of the weight loss takes place at temperatures above this value and up to 900ºC.

Table 4.1.3. Amount of CO and CO_2 released in the TPD in the samples.

Sample	**μmol CO/g AC**	**μmol CO_2/g AC**	**CO/CO_2**
ME	601	245	2.45
ME400	536	186	2.88
ME700	476	47	11.59
ME900	216	29	7.41

In Figure 4.1.7, a comparison between the weight loss of samples ME, ME400, ME700 and ME900 calculated from TGA's and from TPD's is made. Results from both techniques are quite comparables, leading to assume that calculations made from calcium oxalate monohydrate calibrations are valid for the quantification of CO and CO_2 released during TPD's.

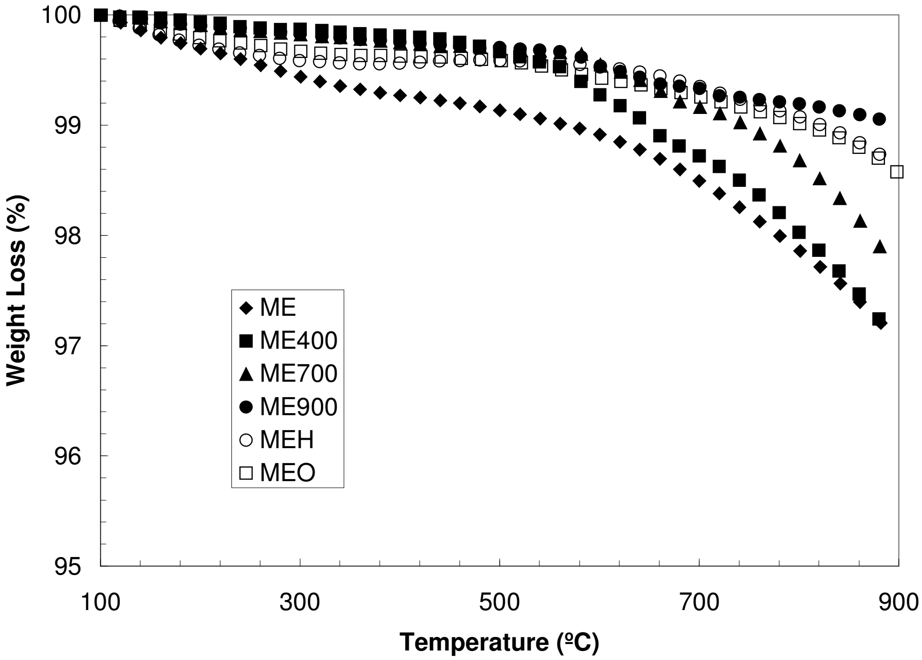


Figure 4.1.6. TGA profiles of the original ME and thermally modified samples.

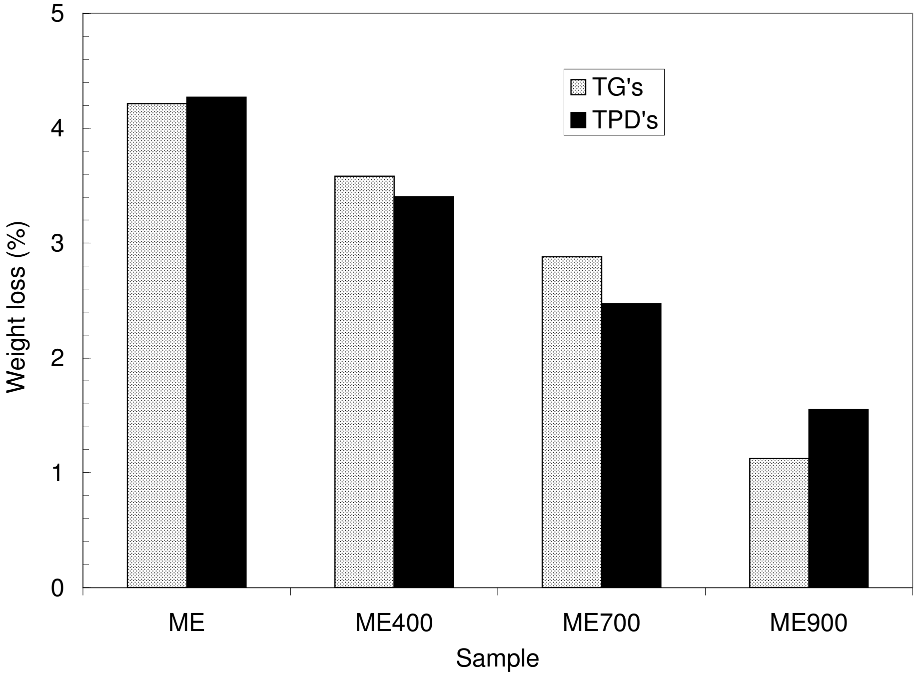


Figure 4.1.7. Quantification of weight loss from TGA's and TPD's.

Table 4.1.4 shows the elemental analysis of the commercial ME and thermally treated ME. As expected, the oxygen content diminishes as the temperature of the treatment increases. The percentage of nitrogen and sulphur remains unaltered by the treatment. Within the experimental error, the variation of hydrogen percentage is not relevant. It must be noted that the oxygen percentage is calculated by difference, so the associated error of this technique is reflected mainly in the oxygen content.

Table 4.1.4. Elemental analysis of all the samples.

Sample	% N	% C	% H	% S	% O[a]
ME	0.56	86.60	0.33	1.08	11.43
ME400	0.55	88.73	0.19	0.91	9.62
ME700	0.55	90.83	0.24	1.09	7.29
ME900	0.55	92.98	0.19	1.03	5.25

[a] By difference

Indeed, there is a difference between the oxygen content from elemental analysis and that calculated by TPD's. In Table 4.1.5, the differences are highlighted. Roughly, TPD seems to account for only 25% of the total oxygen. The discrepancy is partially due to the presence of oxygen in inorganic species contained in the mineral matter. It must be noted that the latter value is 4.5% of the original ME mass, as reported by manufacturer (see Table 4.1.6). But considering that the weight loss calculated by TPD's agrees satisfactorily with the weight loss indicated by TGA (see Figure 4.1.7), the values of elemental content from that analysis should not be taken as accurate. Anyway, the tendency of decrease in oxygen content in samples thermally treated qualitatively supports the other analyses.

Table 4.1.5. Oxygen content calculated from elemental analysis and TPD.

Sample	Oxygen content from elemental analysis (mg/g AC)	Oxygen content from TPD's (mg/g AC)
ME	114.3	30.9
ME400	96.2	24.2
ME700	72.9	17.5
ME900	52.5	11.7

The thermal treatment under hydrogen aims at, on one hand, maximizing the removal of all surface groups by using the reactive hydrogen atmosphere for a longer heat treatment period. On the other hand, hydrogen treatment stabilises the carbon surface due to re-oxidation upon the further exposure of the thermal-treated carbon to the atmospheric air or during the TBR experiments. It is known that during the heat treatment under hydrogen atmosphere, hydrogen partially stabilizes the carbon surface by deactivation of the surface active sites, i.e., forming stable C-H bonds and/or gasification of unstable and reactive carbon atoms found at the edges of the crystallites (Menéndez et al., 1996). Hence, Boehm titration results from MEH show a complete removal of all strong and intermediate acidic groups and existence of only a small amount of weak phenolic groups on the surface of hydrogen treated carbons. This result is supported by the weight loss profile of sample MEH (Figure 4.1.6). When heated up to 900ºC, the most significant weight loss occurs above 700ºC, where phenolics and carbonyls functionalities are decomposed, which according to Table 4.1.2 are the only surface oxygen groups present in this carbon.

The procedure designed for sample MEO achieved mainly two aims at once. The reformation of phenolic functionalities, eliminated by the heating under N_2 up to 900ºC, practically allowed to reach its original value (0.094 vs 0.097 mg/g AC of the parent ME), but maintaining the elimination of the more acidic functionalities (i.e. carboxyls). Thus this sample will allow evaluating the role of predominant phenolic and carbonyl groups of AC in phenol adsorption and in CWAO. The MEO weight loss during TGA displayed in Figure 4.1.6 indicates that this sample only shows an important weight loss above 700ºC, as expected.

The pH_{pzc} of the parent ME and the thermally treated samples is also listed in Table 4.1.2. As discussed in the subsection 3.2.5, to determine the amount of AC mass necessary for the calculation of the pH_{pzc}, first a mass titration was performed. The results are presented in Figure 4.1.8. For a concentration higher than 5% wt, no change in the pH value can be observed. Therefore, all the determinations were conducted using this mass concentration.

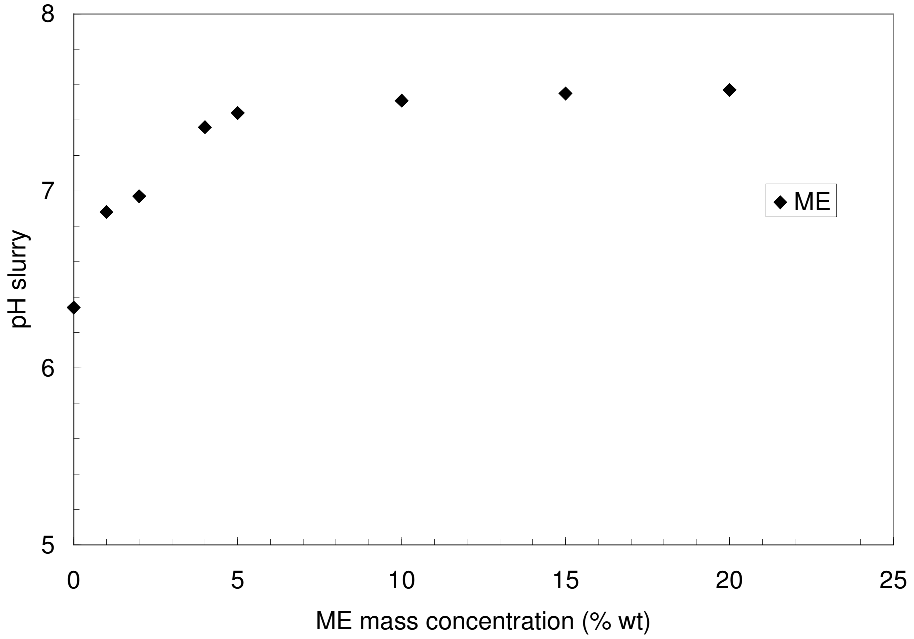


Figure 4.1.8. Mass titration experiment with carbon ME.

The resulting pH increases as the treatment temperature is higher. The slight decrease in carbon acidity with treatment temperature can be due to several factors. In sample ME400, it may be assigned to the removal of the carboxyl groups. The destruction of the carboxyl groups lowers the acidity of the carbon surface and eliminates the neutralisation of the basic groups caused by the interaction between acid and basic groups on the ME surface. This mechanism is responsible for the decreased acidity of ME400. Higher treatment temperatures could also favour the formation of basic groups, like pyrone, chromene and quinone-like groups and this could explain the increased basicity in samples ME700 and ME900. Some of them can be generated by thermal decomposition of oxygenated acidic groups which creates active sites capable of fixing oxygen in ether form, and rearrangement with existing carbonyl groups which resist pyrolysis (Vidic et al, 1997). Also, the increase in basicity of sample ME900 could lie in the formation of pyrone-type basic groups on the surface (Vidic et al, 1997; Tessmer et al. 1997). The very high pH_{pzc} value of the hydrogen treated carbon MEH indicates the high basicity of the carbon surfaces due to almost complete removal of acidic oxygen functionalities. In sample MEO, the total elimination of carboxylic and practically all the lactonic functionalities produces a considerably decrease in its acidity, being its pH_{pzc} higher than the parent ME (9.66 vs. 7.36), despite they have almost the same phenolic oxygen group content.

As previously explained, metal content in sample ME was evidenced during Boehm titrations. Detection of metals was performed to assess their presence. The amount of several metals was measured by ICP. However, only iron and magnesium were detected in significant amounts, but. other expected metals such as copper, chromium, manganese, cobalt or molybdenum were not detected by the ICP. Table 4.1.6 collects these values.

Table 4.1.6. Metal and ash content of carbon ME.

Sample	Ash content (% wt)	Iron content (% wt)	Magnesium content (% wt)
ME	4.5	0.4	0.04

4.1.1.2. Adsorption isotherms

In this section the phenol adsorption performance of carbon ME and the thermally treated samples is discussed. Figure 4.1.9 actually demonstrates that there is no appreciable difference between isotherms performed for contacting time of 2 or 4 hours. Phenol adsorption isotherms of the different activated carbons are shown in Figure 4.1.10. It must be noted that experiments were performed under oxic conditions. Under these conditions oxidative coupling could occur, but due to the short equilibrium time of experiments (2 hours) the phenol polymerisation was not significant.

For all the treated samples, the phenol adsorption capacity increases as the temperature of the thermal treatment increases. This agrees with the generally accepted phenol adsorption mechanism, which is believed to be due to the formation of donor-acceptor complexes between phenol and basic surface groups. In this case, the presence of acidic groups interferes the mechanism, lowering the adsorption capacity.

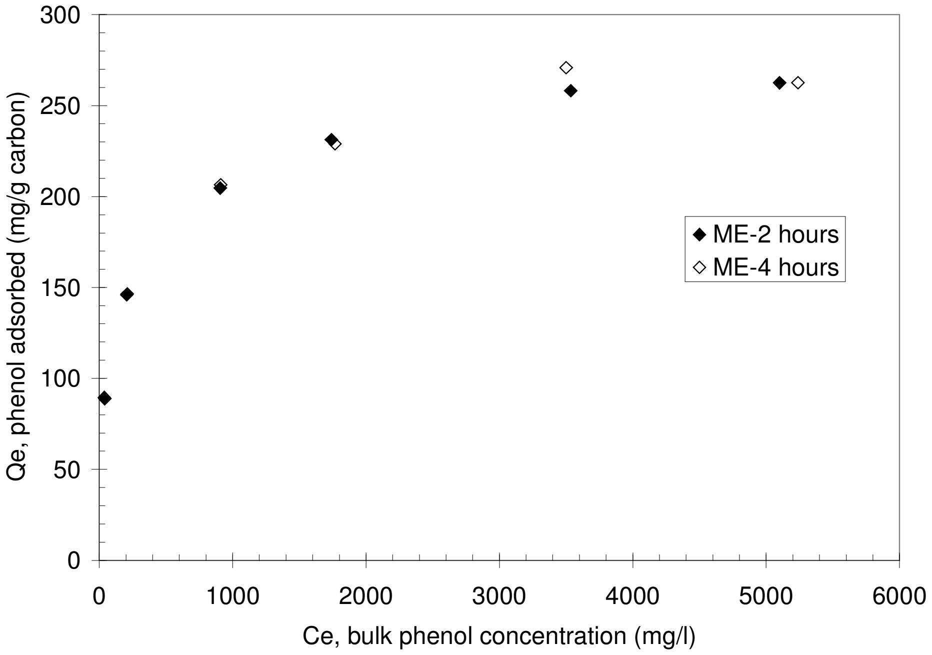


Figure 4.1.9. Phenol adsorption isotherms at 2 and 4 hours.

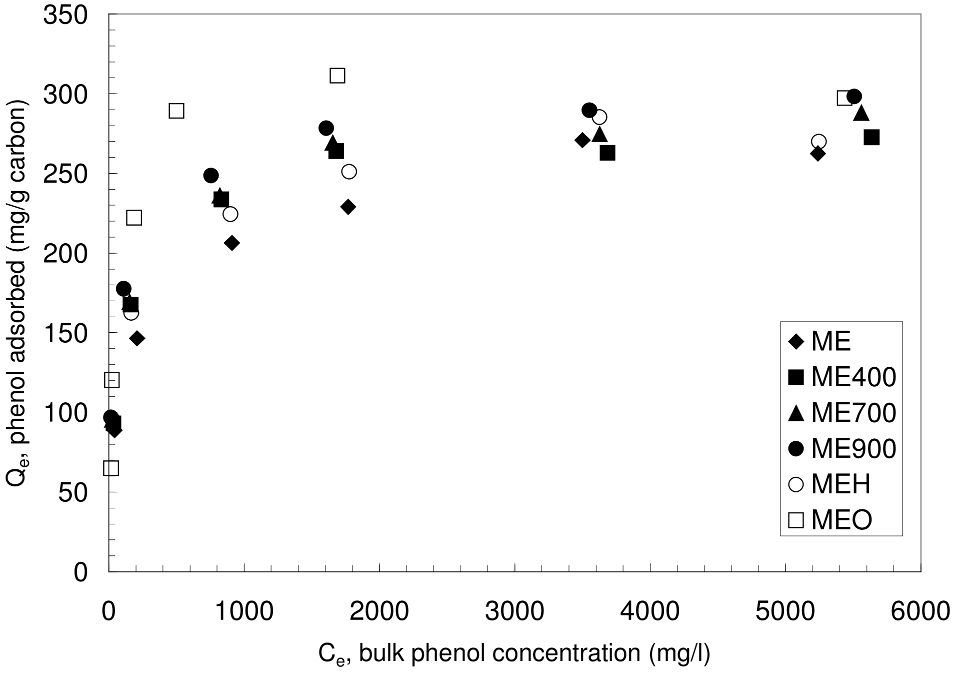


Figure 4.1.10. Phenol adsorption isotherms over activated carbon at 20ºC.

Mattson et al. (1969) studied the nature of the specific interaction between phenol, m-nitrophenol, p-nitrophenol and the surface of AC using infrared reflection spectroscopy. They suggested that phenol and its derivatives adsorb on AC via a donor–acceptor complex mechanism that involves carbonyl surface oxygen groups acting as electron donor, and the aromatic ring of the solute acting as acceptor. This mechanism is generally accepted, but other possible interactions have been proposed. László et al. (2003) proposed three possible mechanisms: (a) electron donor–acceptor interactions between the aromatic phenolic ring and the basic surface oxygens, (b) dispersion effect between the aromatic phenolic ring and the π electrons of the graphitic structure, (c) electrostatic attraction and repulsion when ions are present.

This actually suggests that, in liquid adsorption on solids, the role of the surface functionalities is significantly more determinant than the pore size distribution or the surface area. Looking at the data listed in Table 4.1.1, it can be seen that there is not actual difference between the textural properties of all the samples, as all they have approximately the same surface area and micropore volume. Therefore, the difference in adsorption capacities must be attributed to the different surface oxygen content that they have.

Many research studies concluded that the carboxyl and hydroxyl groups inhibit the adsorption of phenol and increase the affinity of the carbon towards water, so that the solvent molecules could effectively block some micropores. This effect is the so called solvent effect, and can occur when at infinite dilution and neutral pH, the positive surface charge resulting from the adsorption of protons on the strongest surface basic sites leads to the increase in water adsorption, which subsequently blocks some of the most active sites for the adsorption of phenol (Terzyk, 2003).

Accepting that phenol adsorption is governed by π–π dispersion interactions between the basal plane of carbon and the aromatic ring of the phenol, then oxygen bound to the graphite edges can localise electrons and, thereby, remove them from the π-electron system of the basal plane; consequently, the π–π interaction is weakened. Finally, oxygen in the AC surface negatively affects the interaction of electrons between phenol and carbon by making them not available for the aromatic ring.

Overall, a general conclusion is that phenol adsorption is determined not only by π–π interactions and donor–acceptor complex formation but also by the solvent effect. This usually neglected effect, besides the two aforementioned, occurs simultaneously during adsorption and strongly modifies the adsorption properties of the carbons towards phenol (Dabrowski et al., 2005).

The above statements would explain the behaviour of the phenol adsorption capacity for the modified ME. As the temperature of treatment increases, the oxygen surface functional groups are progressively removed, decreasing the surface oxygen content, therefore not only favouring the interaction between the π-electron system of the aromatic plane of AC and the phenolic aromatic rings, but also diminishing the undesired solvent effect, by eliminating acidic surface groups that enhance water adsorption and consequently block the micropore access (and therefore also the active sites access) to phenol molecules.

Inspecting the properties of the thermally treated samples, the higher the temperature achieved, the lower the acidity of the resulting activated carbon. This clearly demonstrates that the thermal treatment effectively remove acidic type groups. Hence, the ME900 and MEH carbons have the lowest acidic group content, as shown by the pH_{pzc} values presented in Table 4.1.2. The lower acidic group content turns into a higher capacity adsorption for ME900 and MEH carbons (Figure 4.1.10).

In addition, if adsorption takes place in unbuffered solutions, like done here, both the phenol and the surface groups could coexist in their protonated and deprotonated forms, depending on their pK_a values ($pK_a = 9.89$ for phenol) (Dabrowski et al., 2005; Terzyk, 2003). All three types of surface-phenol interactions exposed before may simultaneously occur, and all three types of surface-phenol interactions are favoured by the removal of oxygen surface functional groups.

However, at high phenol concentration is also necessary to take into account that adsorbate-adsorbate interactions would predominate, and the phenomena of oxidative coupling may occur. Grant and King (referenced therein Dabrowski et al., 2005) propose the nature and a mechanism for the irreversible adsorption of phenol through oxidative coupling reactions. Their results show that polymerisation of phenol occurred on the surface of AC. The products of the reaction of phenol oxidation included usually dimers, and higher length polymers. In the most cases, oxidation of the phenolic compounds involves removing a hydrogen atom from each phenolic molecule and forming intermediate radicals that join, by carbon–carbon bonds, at the ortho- and/or para- position to the hydroxyl groups.

It has already been established that metals and metal oxides present on the carbon surface are not the key factor responsible for catalysing oxidative coupling of phenols under oxic conditions (Uranowski et al., 1998). Instead, Terzyk (2003) proposed that both oxygen and phenol diffuse to the surface of the carbon and then are adsorbed there, so the reaction occurs on the carbon surface and is catalysed by it.

Tessmer et al. (1997) demonstrated that the presence of acidic surface functional groups inhibits phenolic compounds adsorption under oxic conditions by reducing its effectiveness in promoting adsorption via oxidative coupling reactions. Also, treating samples at temperatures higher than 900ºC causes elimination of oxygen complexes, resulting in more basic carbon that does not contain oxygenated acid groups. Greater structural ordering and delocalized electrons on the carbon surface may increase the carbon basicity but do not enhance its ability to promote irreversible adsorption.

In the adsorption experiments conducted in this research work, the low acidity of the samples treated at 900ºC would favour not only the electron interactions exposed before, but also the oxidative coupling reactions, especially in samples ME900 and MEH. By reducing the acidity in carbon samples also is possible to promote other interactions on the AC surface with phenol, so that this kind of interactions could be responsible for the increase observed in the adsorption capacity at high concentrations of phenol. As the maximum temperature of treatment is 900ºC, not all the oxygenated functional groups are removed (Figure 4.1.5, Table 4.1.2), thus sample ME900 still have oxygen groups in the surface and, considering that adsorption isotherms were performed in oxic conditions, oxidative coupling reactions could have been occurring on the samples surface, increasing the adsorption capacity. However, the short contact time left to equilibrate the samples should not be enough to allow oxidative coupling reactions to take place.

Sample MEO is the only carbon with considerable content of phenolic and lactonic functionalities, but without any carboxylic surface groups. This produces a higher adsorption capacity at the low bulk phenol concentration range than other samples at higher values of bulk concentration. However, the adsorption capacity reaches the same plateau than the rest of the carbons studied. This could be explained if the absence of carboxylic oxygen groups is considered as this avoids the formation of water clusters improving the interaction between the electron pairs of oxygen from carbonyl groups present in lactonic functionalities and phenol aromatic rings, thus forming an electron-donor acceptor complex, which has been proposed as one of the main mechanism for the phenol adsorption over AC.

4.1.1.3. Theoretical models for phenol adsorption

The Freundlich adsorption equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies (Faust and Aly, 1987).

In Table 4.1.7, Freundlich parameters obtained from fitting of experimental data are shown. Although Freundlich is typically used in most of the cases with data at dilute conditions, where no plateau is observed, in this research work, even at the high concentration adsorption experiments, the data was acceptably fitted to this model. This could be due to the presence of a highly heterogeneous surface and the high phenol concentrations conditions that could promote several kinds of adsorption on the carbon. In fact, the stronger the adsorbate-adsorbent interaction, the lower the 1/n value and closer to zero (Furuya et al. 1997). Values in Table 4.1.7 indicate that the adsorption of phenol on carbon ME is favoured by a promoted adsorbate-adsorbent interaction when eliminating acidic functionalities from the surface. This is reflected in very low values of 1/n. In general terms, none of the treatments did have a significant impact on these values.

Table 4.1.7. Freundlich parameters for phenol adsorption of ME and heat treated samples.

Sample	**K (mg/g AC)(l/mg)$^{1/n}$**	**1/n**	**R^2**
ME	40	0.23	0.98
ME400	47	0.23	0.93
ME700	56	0.20	0.95
ME900	64	0.19	0.94
MEH	48	0.22	0.98
MEO	61	0.21	0.94

4.1.1.4. Catalytic performance of ME'scarbons in the TBR system.

The evolution of the phenol conversion in front of the time on stream is shown in Figure 4.1.11 for the CWAO tests of the different samples in the TBR system.

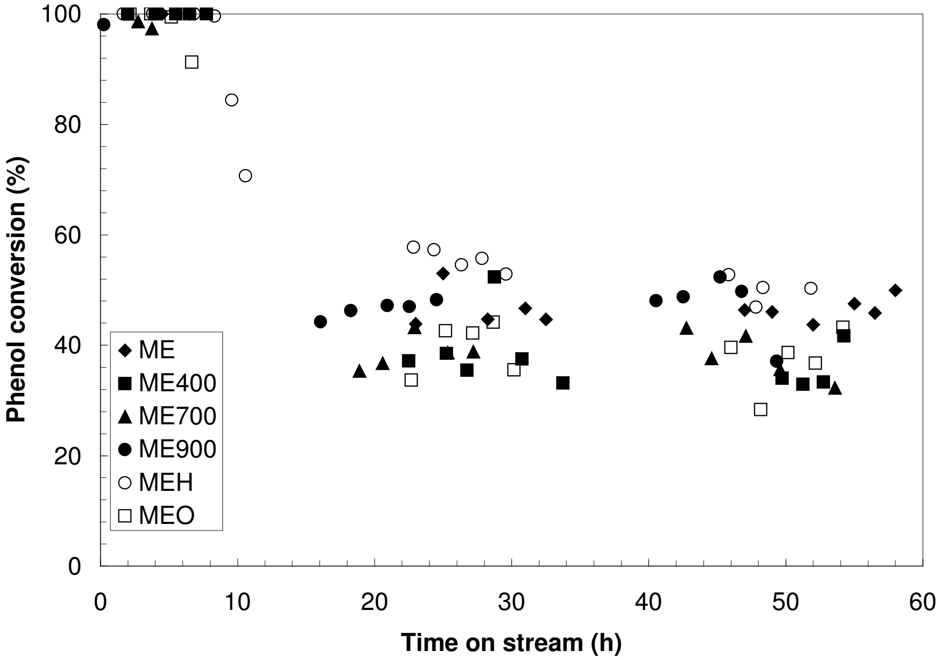


Figure 4.1.11. Phenol conversion in TBR reactor using commercial ME and thermal modified samples, at 140ºC and 2 bar of oxygen partial pressure.

From the start-up and until 5-10 h, adsorption predominates, which results in an apparent total phenol conversion. Once the activated carbon bed reaches a pseudoequilibrium state, phenol conversion drops rapidly to achieve an almost constant phenol conversion, which is then maintained for hours. During this non-steady period, oxidation does exist but the reaction products are also adsorbed in competence with phenol. This hypothesis is confirmed when monitoring the pH values of the exiting liquid effluent. Figure 4.1.12 demonstrates that, despite there is no phenol detected by the HPLC during the first 10 hours of operation, the pH descends from 6.70 down to 3.67 after 7 hours.

The results indicate that thermal treatment at 900ºC, either under N_2 or H_2 slightly increases the phenol conversion, being 45% for the original ME and 49% and 50% for ME900 and MEH, respectively. This may be explained by almost complete removal of surface acidic groups, that were hindering the adsorption of phenol on the carbon surface and, consequently, giving lower phenol conversion. The better performance of MEH, comparing to ME, might be attributed to the more stable surface of the hydrogen treated carbon (Dastgheib et al., 2004) that makes it more resistive to re-oxidation during the TBR operation.

Some reports in the literature can be found that stress on the important catalytic activity of carbonyl and quinone groups for oxidation reactions, for instance the oxidative dehydrogenation of ethylbenzene carried out on activated carbons (Pereira et al., 1999).

However, samples with low acidic surface group content and considerable amount of lactones and phenolic groups, ME700 and MEO, have shown the same catalytic behaviour than original ME. This suggests that the oxidative environment inside the reactor is actually reoxidising the modified AC's, eliminating any possible positive effect of the removal of acidic groups from carbon surface.

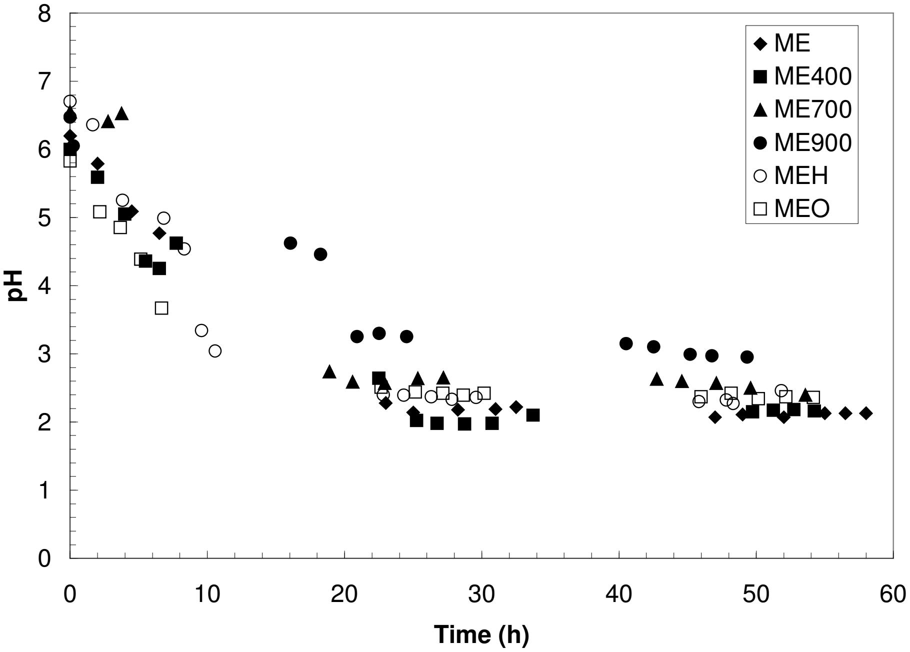


Figure 4.1.12. pH profile of liquid samples from TBR.

Although the slight improved phenol conversion given by ME900 and MEH, this is not significant enough and probably, the possible effect of the surface groups are offset by the re-oxidation occurring at the conditions applied.

As previously stated, the mineralisation of phenol is not complete and partial oxidation products appear in the exited effluent. The analyses of the samples show that ME yields 94% of acidic compounds whereas MEO gives 95%. This indicates that ME's catalysts are capable of oxidising phenol up to acidic compounds, which should be easily degraded by a subsequent biotreatment.

Figure 4.1.13 shows the TOC conversion from CWAO tests in the TBR using commercial ME and its thermal modified samples. Only data for ME, MEH and MEO are available. For a better discussion, the difference between phenol and TOC conversion should be taken into account, because this value represents the selectivity towards carbon dioxide. The lower this difference, the higher the CO_2 selectivity. For ME, the difference is 13%, and 11% for MEH and MEO. These values indicate that thermal treatment neither improved nor decreased the CO_2 selectivity obtained with commercial ME.

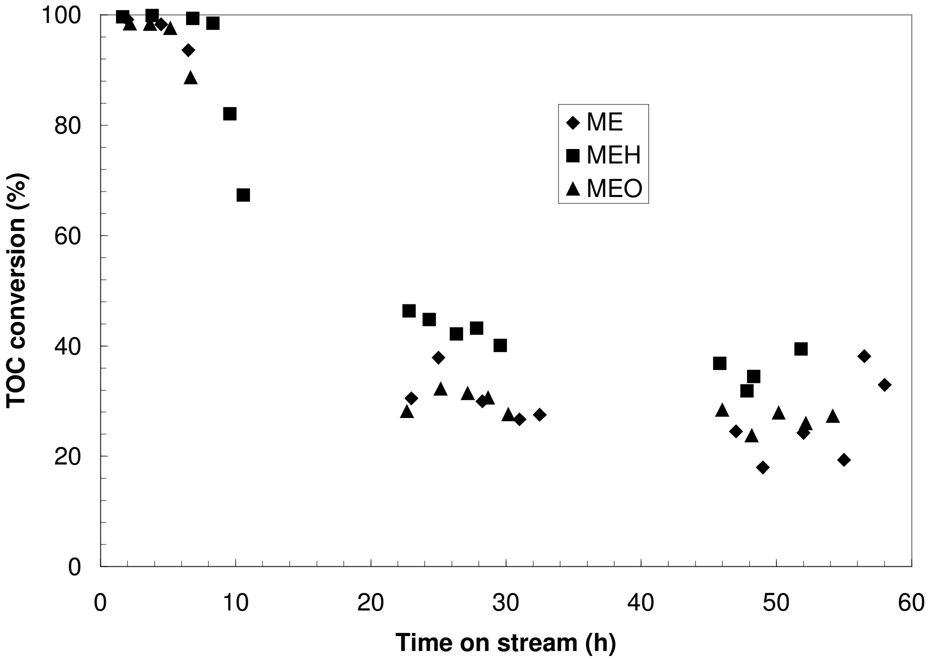


Figure 4.1.13. TOC conversion in TBR reactor using commercial ME and thermal modified samples, at 140ºC and 2 bar of oxygen partial pressure.

4.1.1.5. Characterisation of AC's spent catalysts

Table 4.1.8 summarises the main characteristics of ME and the thermal modified samples after being used as catalyst in the TBR. The most relevant change is the dramatic decrease in the surface area. The micropore volumes calculated from the N_2 and CO_2 adsorption isotherms are similar in samples ME, ME400 and ME700. However, these values are significantly lower compared to those measured before reaction. Also an increase in the amount of CO and CO_2 released during TPD's is found in comparison with the amount released for the non used samples.

Table 4.1.8. AC characterisation of original and the modified AC's after catalytic tests in the TBR.

Sample	SA_{BET} (m^2/g)	V_{mic} D-R N_2 (cm^3/g)	V_{mic} D-R CO_2 (cm^3/g)	µmol CO/g	µmol CO_2/g
TBR-ME	190	0.091	0.080	1274	891
TBR-ME400	199	0.095	0.089	1293	823
TBR-ME700	178	0.086	0.083	1363	810
TBR-ME900	92	0.045	0.075	1285	739

The same trends were elsewhere observed by several researchers. Fortuny et al. (1998) noticed an initial increase in the carbon mass inside the reactor, which they assumed to be due to the formation of phenol condensation products that are difficult to oxidise. Also, Pereira et al. (2001) reported the blockage of the pores in the beginning of the ODH reaction. They even calculated that after 30 min, the carbon had already lost 70%

of its microporosity. In our case, the decrease in microporosity reached 85% for ME and 92% for ME900. The loss in surface area calculated was of 84% for ME and of 93% for ME900. This blockage was attributed to a coke deposition in the surface, which was also responsible for the deactivation of activated carbon catalysts. Santiago et al. (2005) also observed a decrease in surface area in AC when used as catalyst in the phenol oxidation reaction. Also oxidative coupling occurring during the operation in the TBR could contribute to the surface area reduction. Humayun et al. (1998) detected the formation of dimers, specifically, 2,2'-dihydroxybiphenyl, 4,4'-dihydroxybiphenyl, 2-phenoxyphenol, and 4-phenoxyphenol on the carbon surface during aqueous adsorption of phenol. They were identified as common products of the oxidative coupling.

Thus, the loss of surface area can probably be rather assigned to the deposition of phenolic polymers due to condensation over AC surface. Also, the oxidative coupling products could be responsible of the pore blockage, making them inaccessible for N_2 and CO_2 during the adsorption isotherm analysis. As a result, this leads to a decrease not only in surface area but also in the microporosity reported in Table 4.1.8. An increase in the release of CO and CO_2 from all the samples, if compared with the non used ME's (see Table 4.1.3 and Table 4.1.8), supports the hypothesis that there are compounds attached to the AC surface. The weight gained in the used ACs after 55 hours of operation is listed in Table 4.1.9, as well as the final pH of the liquid effluent in each experiment. Since the pH profiles are similar in all the TBR experiments done, in next sections only the final pH on stream for each carbon is given. The figures for all experiments can be found in the Annex A.

Table 4.1.9. Weight difference in ME's samples after operation in TBR and final pH of liquid stream.

Sample	**ΔW (g)**	**Final pH on stream**
ME	2.519	2.13
ME400	2.387	2.16
ME700	2.670	2.40
ME900	2.680	2.51
MEH	2.400	2.46
MEO	2.664	2.36

Figure 4.1.14 shows that the weight losses of all the samples after 55 hours on stream are practically identical. Considering that all the samples have the same weight loss, the assumption that a final homogenisation of all ME samples due to re-oxidation and oxidative coupling phenomena is again supported.

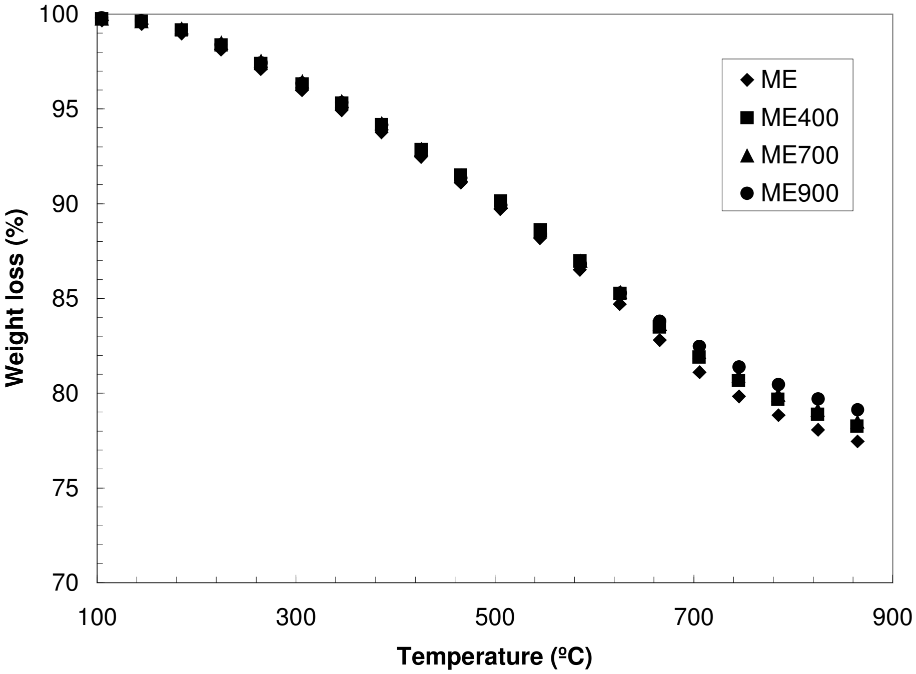


Figure 4.1.14. Weight loss for original and modified ME's after being used as catalyst.

4.1.2 Thermal treatment on carbon HD and HDDS

4.1.2.1. Physical and chemical characterisation

Surface area and porosity data collected in Table 4.1.10 indicate that HD is a mesoporous activated carbon. The objective of steam treatment was to enhance even more the porosity while hydrogen treatment was aiming at removing surface functionalities, particularly oxygen-containing acidic groups, and stabilize the carbon surface for resistance to re-oxidation upon the exposure to the atmospheric air or during the adsorption/wet oxidation experiments. Data show that steam treatment had a more significant impact on surface area and porosity of carbons than hydrogen treatment and demineralization. Nitrogen adsorption isotherms depicted in Figure 4.1.15 also demonstrate that the increase of surface area and pore volume achieved with steam treatment was considerably higher than with the acid wash for demineralisation. Surface area in the latter case, HDD, is 20% higher than the original HD, whereas in the case of steam treatment (HDDS) the increase is about 54%. Porosity also was affected by the modification treatments conducted on HD. The total pore volume increased only 10% in sample HDD, but a considerably 32% for HDDS, demonstrating that steam treatment was indeed the modification that provided more changes in the textural properties.

Table 4.1.10. Physical properties of parent and modified HD.

Sample	**SA_{BET} (m^2/g)**	**V_{mic} D-R (cm^3/g)**	**$V_{mes+mac}$ (cm^3/g)**	**V_{tot} (cm^3/g)**
HD	681	0.279	0.495	0.774
HDD	816	0.337	0.515	0.852
HDDH	732	0.301	0.488	0.789
HDDS	1046	0.429	0.591	1.020
HDDSH	1018	0.403	0.594	0.997

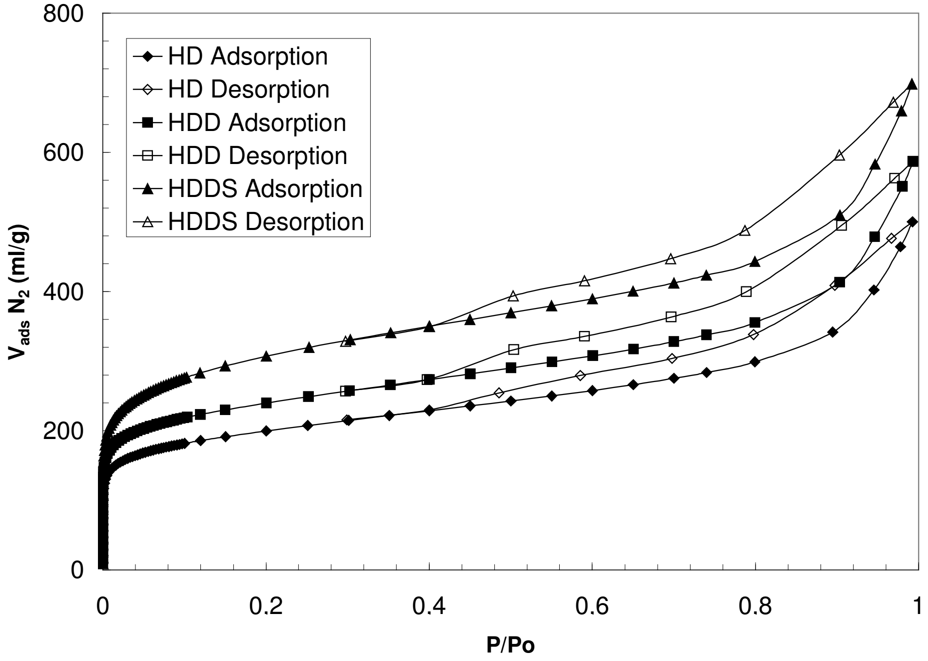


Figure 4.1.15. N_2 adsorption isotherms on carbon HD, demineralised HDD and steam treated HDDS.

Nitrogen adsorption isotherm shapes in Figure 4.1.15 match Type IV of the IUPAC classification. The hysteresis loop indicates the presence of mesoporosity at some extent. This hysteresis is due to the difference between the mechanism of mesopore filling by capillary condensation and the mechanism of mesopore emptying (Marsh and Rodríguez-Reinoso, 2006). In fact, 64% of the porosity of sample HD is in the mesopore range. It is important to notice that, despite the demineralization treatment and steam treatment modify the textural properties of parent HD, so that the pore volume increased in both cases, the proportion of mesopores in all samples was not dramatically changed. As abovementioned, 64% of the porosity of HD was in the mesopore range, and slightly decreased at 60% and 58% for HDD and HDDS respectively. Therefore, most of the new porosity appeared in the micropore range.

The objective of acid treatment was to remove minerals (particularly iron) that, as previously suggested, could have some impact on the catalytic activities of carbon. The iron and oxygen surface functionalities contents of the set HD are listed in Table 4.1.11.

Table 4.1.11. Chemical characteristics of HD samples.

Sample	**Phenolics (meq/g)**	**Lactones (meq/g)**	**Carboxyls (meq/g)**	**pH_{pzc}**	**Iron content (% wt)**
HD	0.000	0.102	0.407	5.22	0.06
HDD	0.000	0.356	0.260	4.01	0.03
HDDH	0.061	0.000	0.051	9.41	n.m.[a]
HDDS	0.000	0.928	0.074	7.55	0.03
HDDSH	0.000	0.081	0.005	10.17	n.m.[a]

[a] Iron content of HDDH and HDDSH is about that of the HDD (i.e., 0.03% wt).

Values of pH_{pzc} and surface oxygen content from Boehm titrations from Table 4.1.11 reveal that HD has a slight acidic to neutral surface. Demineralisation, i.e. HDD, had a moderate impact on the surface acidity, in spite of increasing up to 3.5 times the original content of lactonic functionalities. High temperature steam treatment, HDDS, drove the surface to the basic zone. In this case, despite the drastic increase of lactonic groups, the almost complete elimination of carboxylic functionalities renders an slightly basic surface, as its pH_{pzc} indicates. In all cases, hydrogen treatment produced a highly basic surface. However, the highest elimination of acidic functionalities, reflected in the higher pH_{pzc}, was achieved in sample HDDSH. High temperature hydrogen treatment dissociates the majority of the surface oxygen groups and significantly decreases surface polarity. The iron content of these demineralised samples was approximately half of the original value for all them.

The characterisation of the surface was also assessed by TGA. For instance, the weight loss of samples HDDS and HDDSH are drawn in Figure 4.1.16. The absence of the carboxylic groups that decomposes below 400ºC can be clearly appreciated in sample HDDSH. The lower content of lactonic functionalities that decomposes below 700ºC is also observed in the profile of sample HDDSH. Both samples showed weight losses above 700ºC, where carbonyls and quinones decomposed according to the literature. These groups were not directly measured by Boehm titrations, but rather they are considered included in the phenolic type of groups. However, their presence again demonstrates that, as previously observed for ME samples (Figures 4.1.3 and 4.1.4), the treatment up to 900ºC did not actually eliminate all the surface oxygen functionalities.

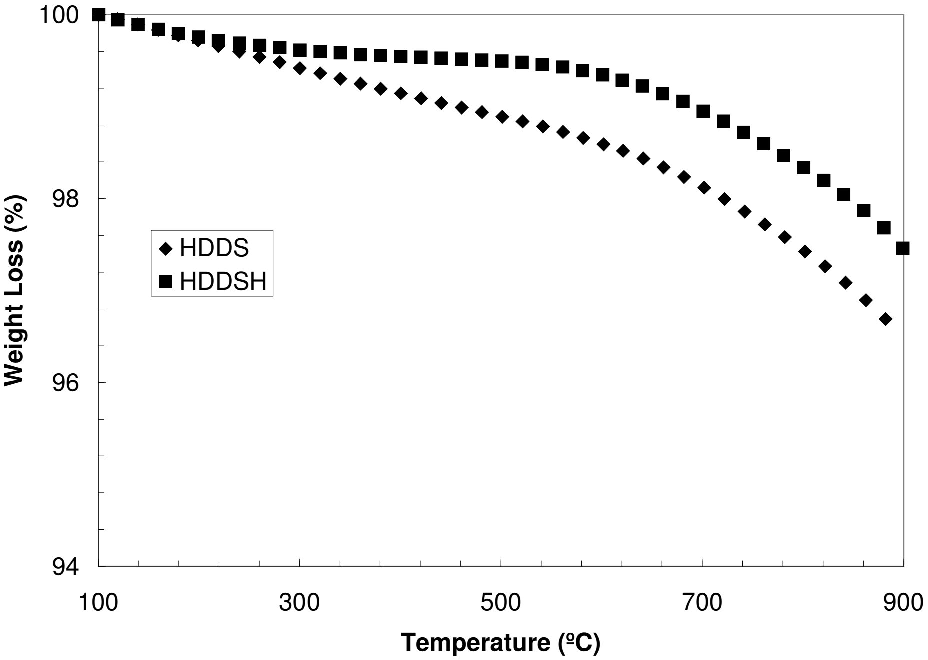


Figure 4.1.16. TGA profiles of the original HDDS and thermally modified sample HDDSH.

4.1.2.2. Adsorption isotherms

Phenol adsorption isotherms for the set HD of activated carbons are shown in Figure 4.1.17. Overall, the highest phenol removal was found for HDDSH, primarily due to its higher micropore volume compared with the other carbons of the group (nearly 45% higher than for the parent HD), and also due to the lower presence of oxygen functionalities. As already commented, oxygen functional groups impart hydrophilicity to the surface that could form water clusters and block the access of phenol molecules to pores. The highest phenol adsorption capacity of samples HD, HDD and HDDH is generally around the same value, 280 mg/g AC. The lowest adsorption capacity is shown by carbon HDDS, which also shows the highest surface oxygen content resulting from the steam treatment. In this case, the improvement of the microporosity, which should favour the phenol adsorption, is largely offset by the higher hydrophilicity of its carbon surface, on the whole decreasing the adsorption capacity down to 96 mg/g AC.

Table 4.1.12 collects the Freundlich parameters after fitting of the adsorption isotherms. As discussed in the subsection 4.1.1.3, the 1/n Freundlich parameter reflects the affinity of the surface adsorbent towards the adsorbate. For all samples, except HDDS, the 1/n values are relatively low, indicating a favoured interaction between phenol molecules and carbon surface. Sample HDDS, shows the lowest 1/n, which could suggest a better interaction phenol-AC surface than with the rest of carbons from this set, but the value of R^2 from the adjustment indicates that in this case the Freundlich model did not fitted very well the experimental data, so that this statement must be cautiously taken.

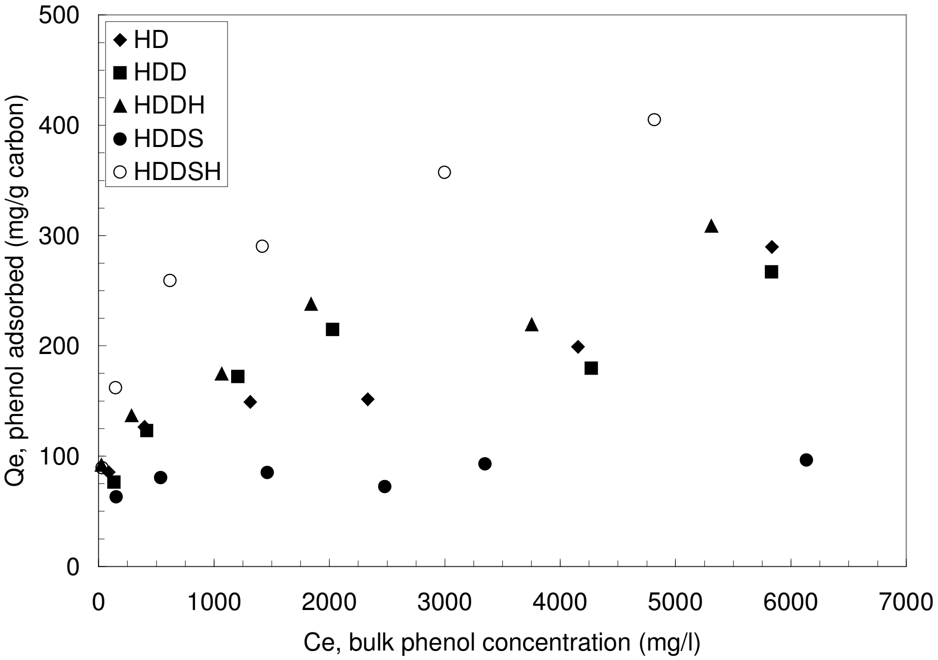


Figure 4.1.17. Adsorption isotherms of phenol by HD activated carbons at 20ºC.

Table 4.1.12. Freundlich parameters for phenol adsorption of HD and heat treated samples.

Sample	**K (mg/g AC)(l/mg)$^{1/n}$**	**1/n**	**R^2**
HD	36	0.20	0.95
HDD	20	0.29	0.89
HDDH	46	0.22	0.96
HDDS	40	0.10	0.66
HDDSH	36	0.29	0.98

4.1.2.3. Catalytic performance of HD's carbons in the TBR system.

The results of CWAO of phenol in the TBR system are shown in Figure 4.1.18. Similarly than for ME carbons, phenol disappearance during the first 10 hours of operation must be primarily imputed to the adsorption due to the progressive equilibration of the activated carbon bed, while later phenol removal, beyond 20 hours when a steady state is reached, can be mostly attributed to catalytic oxidation. It must be firs commented that, in spite of the high mesoporosity of these samples, the phenol conversion achieved are roughly below that given by ME. Therefore, mesoporosity did not appear to be a critical factor for the catalytic performance in CWAO applications, although some impact does have.

Samples HD and HDD approximately show the same phenol conversion at steady state, between 25 and 30%. High temperature thermal treatment of HDD under hydrogen (HDDH) did not improve the performance of the activated carbon, since the phenol conversion achieved was about 22%, even lower than 25% given by the parent HD. Also, Figure 4.1.18 proves that steam treatment over HDD did not considerably improve the phenol conversion despite the considerable increase of the micropore volume already commented. The results indicate that the most significant change in catalytic activity is observed after the hydrogen thermal treatment performed over the HDDS sample, then giving HDDSH. The conversion obtained with HDDSH increased up to 40%, well above of that obtained with HDDS, 23%. This increase in phenol conversion could be explained by the oxidative coupling phenomena explained in the subsection 4.1.1.5 for carbon ME) According to Terzyk (2003), the presence of acidic surface functional groups inhibits phenolic compounds adsorption under oxic conditions by reducing its effectiveness in promoting adsorption via oxidative coupling reactions. It was demonstrated, through the characterisation of carbons ME after use as catalyst, that the carbon surface after a thermal treatment actually is re-oxidised inside the reactor. Considering that carbon HDDSH has a high mesopore volume free of oxygen functionalities, oxidative coupling reactions could be enhanced and the polymeric chains adsorbed and deposited on the HDDSH mesoporosity, resulting on a higher phenol conversion. As this phenol conversion is maintained over the period 20-50 hours, these phenolic chains should undergo further oxidation, then giving the classical partial oxidation products.

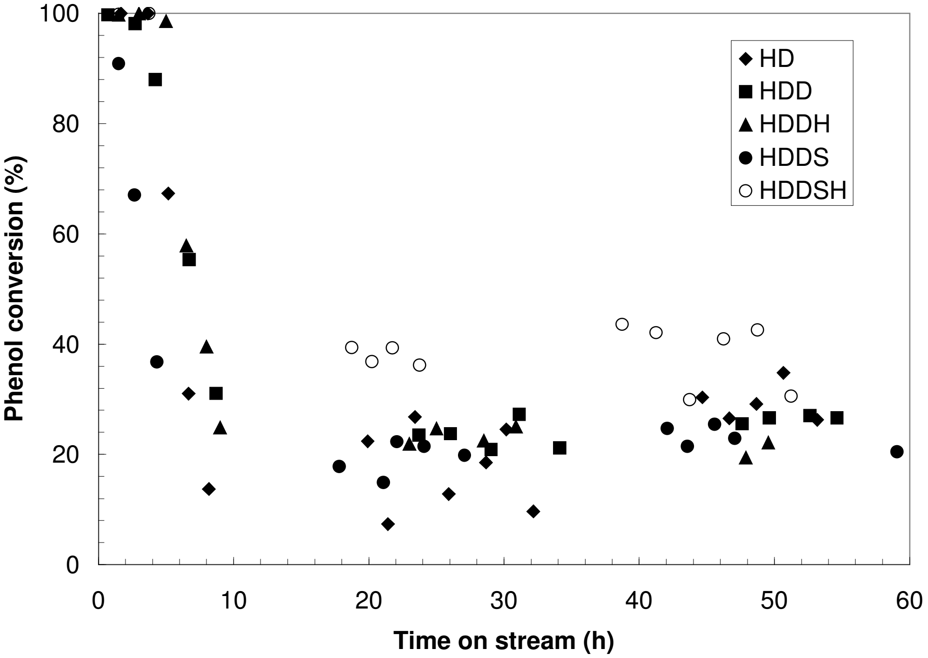


Figure 4.1.18. Phenol conversion in TBR reactor using commercial HD and thermal modified samples, at 140ºC and 2 bar of oxygen partial pressure.

When analysing the TOC conversions obtained with HD's carbons, depicted in Figure 4.1.19, and its difference with the corresponding phenol conversions, several asseverations can be made. In general terms, only sample HDDSH shows a different behaviour in comparison with those obtained from the rest of carbons. Whereas the

TOC conversion for HDDSH is about 25%, the other samples achieved an average of 20%. However, as aforementioned, the difference between phenol conversion and TOC conversion is an indicator of the CO_2 selectivity of the oxidation, so this difference is the factor what should be compared. Despite the highest phenol conversion achieved by HDDSH, the lowest difference, i.e. the higher CO_2 selectivity, was found for HDDH, being these differences 20% and 1%, respectively. The higher difference between phenol and TOC conversions obtained for HDDSH agrees with a different oxidation pathway, as the phenolic chains are expected to be subsequently broken down by oxidation in fragments of still considerably TOC, which then can progress towards complete mineralisation.

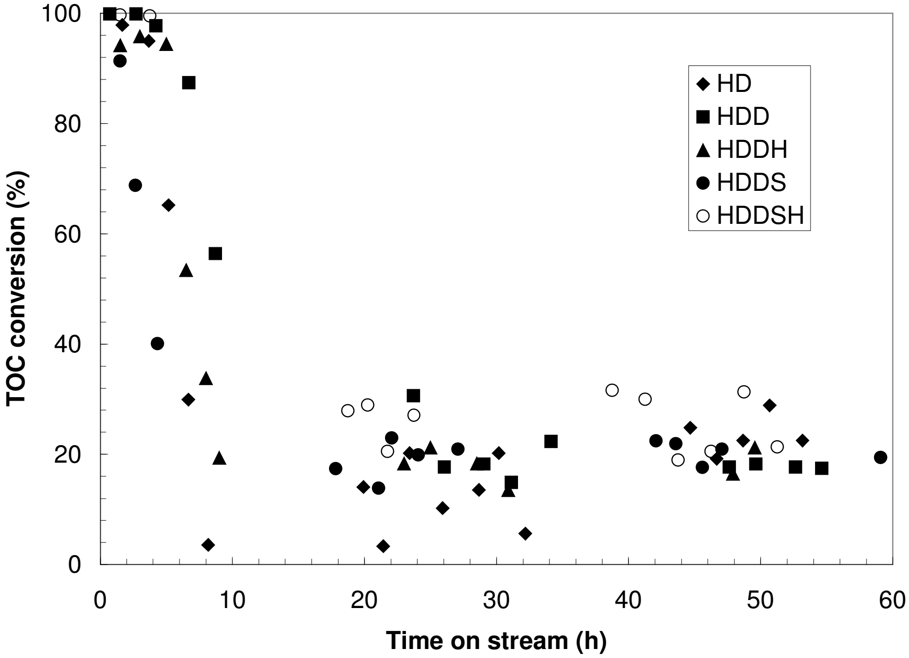


Figure 4.1.19. TOC conversion in TBR reactor using commercial HD and thermal modified samples, at 140ºC and 2 bar of oxygen partial pressure.

Finally, the ΔW of all HD's samples and the final pH of the exited effluent are collected in Table 4.1.13. Low values of pH demonstrate the formation of highly acidic intermediates from phenol oxidation, whereas the positive values of ΔW suggest that there is actually deposition of compounds onto the activated carbon, which turn out in an increase of the final weight. The increase of weight is more relevant for the two hydrogenated samples, HDDH and HDDSH. For this latter, this matches well with the proposed oxidation pathway through the formation of phenolic polymers attached to the activated carbon. The correspondence of the weight gain and the occurrence of attached phenolic chains is supported by the TGA data shown in Figure 4.1.20, where most of desorbed species appear around 500ºC, which could be assigned to cracking of hydrocarbons.

Table 4.1.13 Weight difference in HD's samples after operation in TBR and final pH of liquid stream.

Sample	**ΔW (g)**	**Final pH on stream**
HD	1.34	2.32
HDD	1.26	2.45
HDDH	1.56	2.46
HDDS	1.38	2.40
HDDSH	1.47	2.48

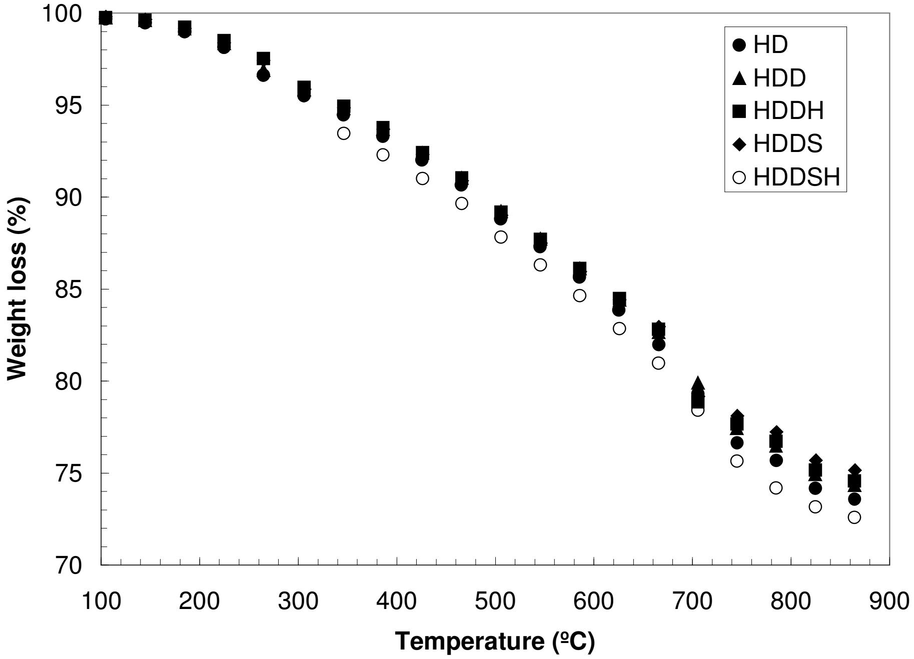


Figure 4.1.20. Weight loss for original and modified HD's after being used as catalyst.

4.1.3. Thermal treatment on carbon WV1 and WV2

4.1.3.1. Physical and chemical characterisation

Samples WV1 and WV2, as mentioned in section 3.1, are activated carbons made from wood. They textural properties are listed in Table 4.1.14. Since it was not possible to make the characterisation by nitrogen adsorption isotherms, the data of surface area and iodine number provided by the manufacturer are included in Table 4.1.14. According to this information, both carbons has a high surface area, higher than the carbons used in the previous sections dedicated to ME and HD, however most of the porosity fall on the range of microporosity. Despite the iodine number cannot be numerically related to the microporisity, it is known that the adsorption of iodine preferentially occurs in the micropores, following a pore filling mechanism, and by capillary condensation when adsorption happens in mesopores (Marsh and Rodríguez-Reinoso, 2006). Then, it is possible to assume that a high value of iodine number is indicative of high microporosity. Consequently, WV1 and WV2 can be considered as highly microporous carbons. Despite being made of the same raw material (wood), they present a very different distribution of surface oxygen groups. Since sample WV2 was treated to decrease its phosphorous content, a high concentration of carboxylic groups was detected, whereas practically neither lactones nor phenolics were encountered by Boehm titration. Hydrogen treatment effectively removed surface oxygen functionalities from carbons, as Boehm titrations and also TGAs (Figure 4.1.21) indicate. However, carboxyls were more efficiently removed as they vanish for WV1 and are lowered from 1.317 to 0.184 meq/g, over 85%, for WV2. Instead, lactones in WV1 were more reluctant but they were still halved. It is surprising that the pH_{pzc} of the parent WV2 was basic given the high concentration of carboxyls.

Table 4.1.14 Physical and chemical properties of parent and modified WV1 and WV2.

Sample	**SA_{BET} (m^2/g)**	**Iodine number (mg/g AC)**	**Phenolics (meq/g)**	**Lactones (meq/g)**	**Carboxyls (meq/g)**	**pH_{pzc}**
WV1	1400-1600[a]	900[a]	0.000	0.690	0.165	6.20
WV2	1400-1800[a]	1200[a]	0.000	0.000	1.317	8.35
WV1H	na	na	0.000	0.349	0.000	9.09
WV2H	na	na	0.000	0.000	0.184	9.93

[a] Information provided by manufacturer.

The increase of the pH in the hydrogenated samples WV1H and WV2H also reflect the successful removal of acidic functionalities from carbon surface since it increased from 6.20 to 9.09 for WV1 and a more moderate 8.35 to 9.93 for WV2. The huge weight loss observed for WV1 is suspected to be related to the presence of residual activation agent, but this speculation cannot be checked as the manufacture process is not known. TGA profile for WV1H supports the reduction of lactonic groups after hydrogen treatment. These groups mainly decomposed between 400 and 700ºC, which are actually the temperatures of higher weight loss in sample WV1. The difference between WV2 and WV2H is not easily perceived in the TGA profile, since carboxylic groups are mainly present in those carbons (Table 4.1.14) and these groups decomposed below 400ºC.

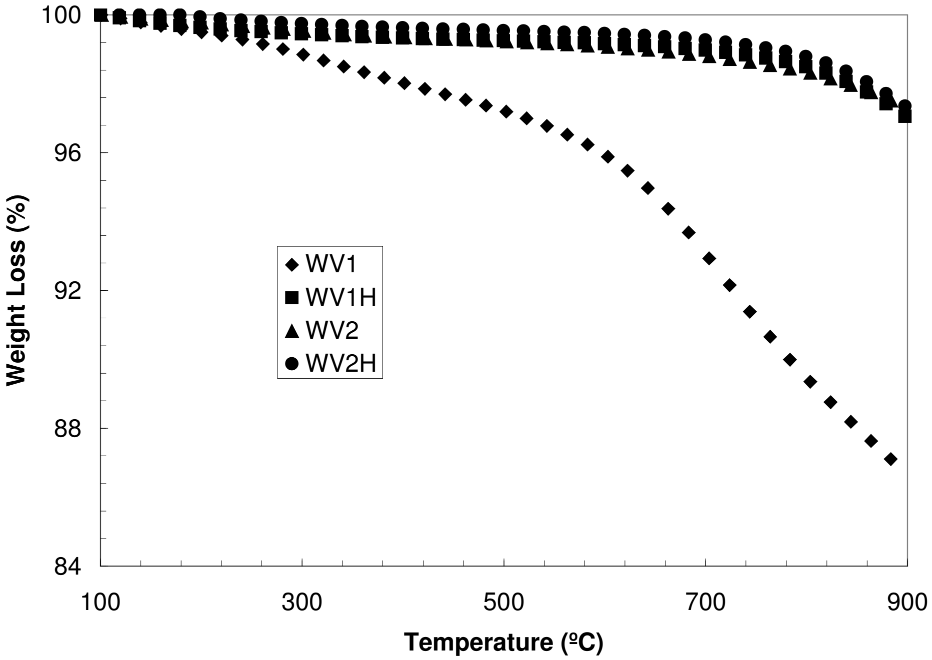


Figure 4.1.21. TG profiles of the original WV1 and WV2 and thermally modified samples.

4.1.3.2. Adsorption isotherms

Figure 4.1.22 depicts the phenol adsorption isotherms obtained for the WV's set of carbons. Adsorption isotherm of ME is included for comparative purposes. The maximum adsorption capacity of original WV1 and WV2 is almost identical, 336 and 340 mg/g AC, respectively. Both parent WV1 and WV2 have phenol adsorption capacity 28% higher than ME. This fact agrees with the higher surface area assumed for WVs.

In both cases, the adsorption capacity significantly increases after hydrogen treatment, 37% for WV1H and a lesser 11% for WV2H. This difference could be attributed to the fact that WV2H still has carboxyls in the surface. These groups are highly hydrophilic, attracting water molecules forming water clusters, thus decreasing the availability of adsorption sites for phenol. On the contrary, WV1 also had carboxylic groups, but they were totally eliminated after hydrogen treatment, so that WV1H posses a more hydrophobic surface than that of WV2H.

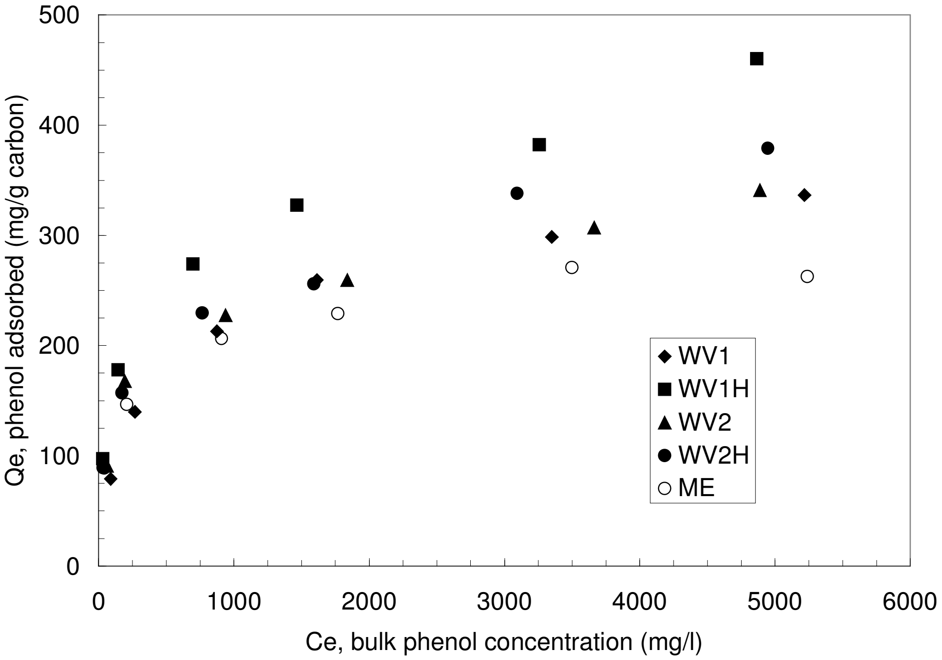


Figure 4.1.22. Adsorption isotherms of phenol by using commercial WV's and thermal modified samples at 20ºC

Table 4.1.15 summarises the Freundlich parameters after fitting of the adsorption data. R^2 values are higher than 0.96 in all the cases, which demonstrates a good adjustment to the model. As for ME, the very low 1/n values indicate a high affinity between the phenol and the carbons surface.

Table 4.1.15. Freundlich parameters for phenol adsorption of the WV's set of carbons.

Sample	**K (mg/g AC)(l/mg)$^{1/n}$**	**1/n**	**R^2**
WV1	19	0.35	0.97
WV2	33	0.28	0.96
WV1H	38	0.29	0.99
WV2H	35	0.28	0.99

4.1.3.3. Catalytic performance of WV's carbons in the TBR system.

Phenol conversion profiles for the WV's set of carbons are plotted in Figure 4.1.23. It is noteworthy that during the first 10 hours of operation, WV's carbons were not able to retain phenol from the liquid stream. As it can be seen in Figure 4.1.23, phenol concentration just after 5 hours of operation already reached 2500 mg/L, i.e. 50% of conversion when using WV1 and WV1H. This trend was not so evident for WV2 and WV2H, but still the equilibration time of the activated carbon bed was lower than expected if the time needed to reach equilibrium is estimated using the maximum adsorption capacity given in Figure 4.1.22 and the TBR operation conditions. This predicted time is 8.5 h, that is indeed higher than the experimentally observed. Given the intrinsic adsorption capacity, maybe kinetic considerations in the adsorption process, due to their high microporosity, can explain the short time during which no phenol exited the reactor. In any case, the conversion obtained with both WV1 and WV1H at steady state is very low, 9 and 11% respectively. The phenol conversion was slightly better, 16%, for both WV2 and WV2H. It must be noted that, since these carbons are made from wood, no iron content was detected for both WV1 and WV2. This is a distinctive trend in comparison with the previously ME's and HD's and suggested that iron presence was a critical factor in their catalytic performance in CWAO.

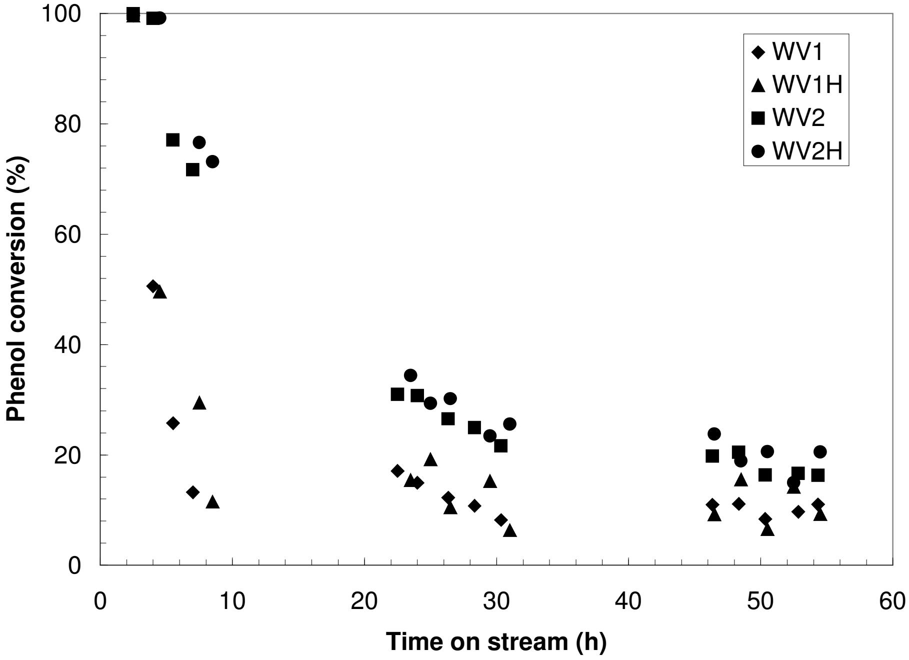


Figure 4.1.23. Phenol conversion in TBR reactor using commercial WV's and thermal modified samples, at 140ºC and 2 bar of oxygen partial pressure

The acidic pH of the exited effluent, listed in Table 4.1.16, indicates the presence of acidic partial oxidation products from the phenol, as expected. Also, the positive ΔW in all the cases suggests the deposition of condensation phenolic compounds over the carbon surface. The increase is comparable to those obtained for ME's carbons and almost twofold those measured for HD's.

Table 4.1.16. Weight difference in HD's samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
WV1	2.433	2.52
WV2	2.727	2.32
WV1H	2.563	2.43
WV2H	2.836	2.29

TOC conversion evolution in front of the time on stream for WV's carbons is shown in Figure 4.1.24. The difference between phenol and TOC conversion is almost nil in all the cases. This indicates a high mineralisation. However in all cases, the presence of intermediates, although low, was in the four cases favoured towards aromatics, 73% and 76% for WV1 and WV2 respectively and 74% and 75% for WV1H and WV2H. This indicates that the catalytic activity of these carbons do not promote the formation of acids from the oxidation of the aromatic compounds form.

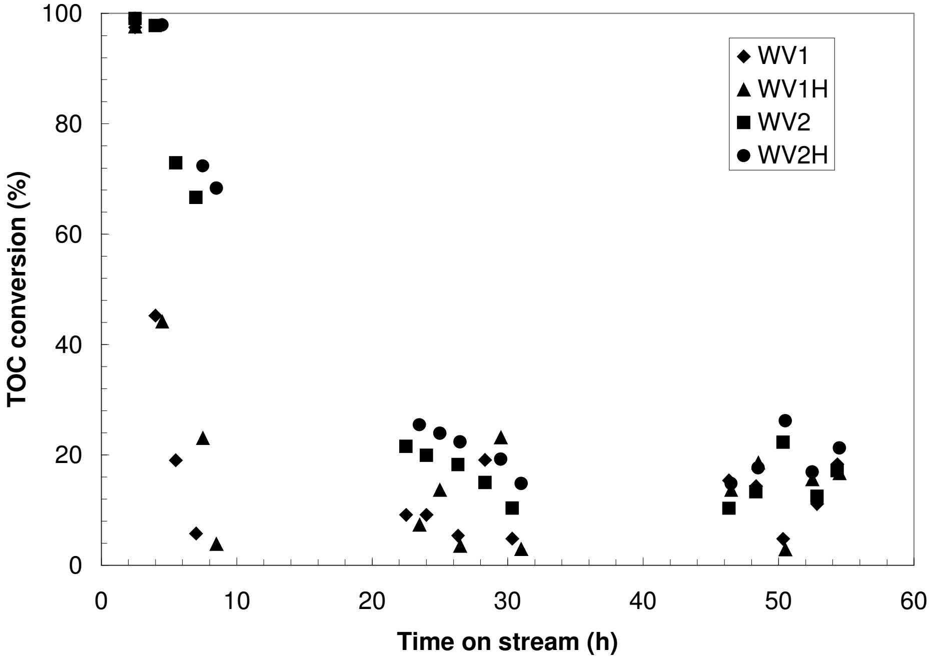


Figure 4.1.24. TOC conversion in TBR reactor using commercial WV's and thermal modified samples, at 140ºC and 2 bar of oxygen partial pressure.

4.2. Commercial activated carbons

4.2.1. Physical and chemical characterisation

The textural properties of all commercial activated carbons are collected in Table 4.2.1. Surface areas are quite comparable, being in the range 800-1200 m^2/g. An exception must be noted for GT with a remarkable low surface area of 681 m^2/g. Although pore volumes are not available for all the samples, available information let to assume that these carbons are mostly microporous.. In the case of ME and F400, microporosity represents more than 75% of the total porosity.

Table 4.2.1. Physical properties of commercial activated carbons.

Sample	SA_{BET} (m^2/g)	V_{mic} D-R (cm^3/g)	$V_{mes+mac}$ (cm^3/g)	V_{tot} (cm^3/g)	Iodine number (mg/g AC)
ME	1261	0.473	0.137	0.610	n.m.
CN	800[a]	n.m.	n.m.	n.m.	800[a]
F400	1035[b]	0.404[b]	0.149[b]	0.553[b]	1050[a]
IR	900[a]	n.m.	n.m.	n.m.	900[a]
GT	602[c]	n.m.	n.m.	n.m.	n.m

[a] Information given by manufacturer.
[b] Data from Dastgheib et al., 2004.
[c] Data from Santiago et al., 2005.

The chemistry of the surface is illustrated in Table 4.2.2, including iron content. All these commercial carbons are rather few functionalised, then giving a basic pH. Only CN has a noticeable acidic character due to its higher content of carboxylic groups. F400 and IR exhibit a more basic character than ME despite their higher content of carboxyls. This probably could be explained by their lower content of phenolics and lactones, compared to ME. In all the samples from mineral origin, iron have been measured at substantial concentrations, between 0.2 and 0.4% wt. In contrast, no iron was detected for GT, which is made from coconut shells.

Table 4.2.2. Chemical properties of commercial activated carbons.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH_{pzc}	Iron content (%wt)
ME	0.097	0.123	0.031	7.36	0.40
CN	0.030	0.000	1.116	6.67	0.38
F400	0.013	0.058	0.190	8.49	0.21
IR	0.015	0.075	0.206	9.00	0.20
GT	0.000	0.021	0.193	9.19	0.00

4.2.2. Adsorption isotherms.

Figure 4.2.1 shows the phenol adsorption isotherms for these commercial activated carbons. F400 shows the highest maximum capacity, 340 mg/g AC. The lowest was obtained with sample ME, 260 mg/g AC. However, the difference is only around 30%. The other three activated carbons, CN, IR and GT, showed intermediate adsorption capacities. In general, it is possible to attribute their rather high adsorption capacity to the high values of surface area and elevated microporosity. In addition, the low amount of acidic functional groups, and the so related high pH_{pzc} could be favouring the phenol adsorption. Due to the low surface affinity for water, the solvent effect is less pronounced and the interactions responsible for the phenol adsorption over the AC are enhanced. Sample GT, in despite of having the lowest value of surface area, shows a considerable phenol adsorption capacity, 20% higher than that found for ME (taken at about 5000 mg/L of equilibrium bulk concentration). Even without knowing the actual pore volume and distribution, this suggests that GT is actually highly microporous, as exhibits an adsorption capacity comparable to that of ME, which surface area is over two times greater.

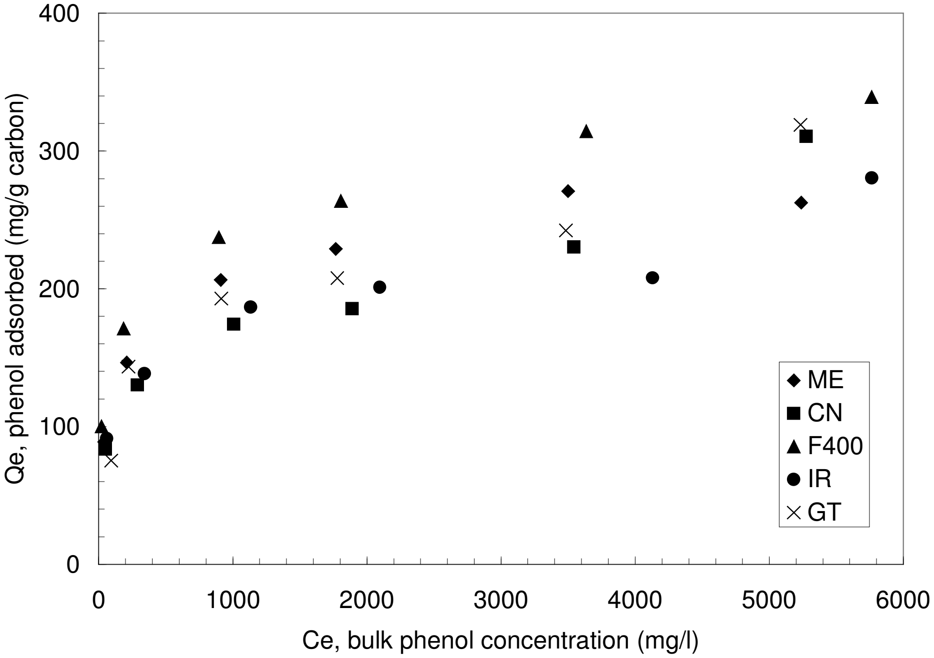


Figure 4.2.1. Adsorption isotherms of phenol by several commercial activated carbons at 20ºC.

Table 4.2.3 summarises the Freundlich parameters for all the adsorption isotherms. As in the previous cases, the very low 1/n values reveal a very high affinity between the phenol and the activated carbon surface.

Table 4.2.3. Freundlich parameters for phenol adsorption of the commercial set of carbons.

Sample	**K (mg/g AC)(l/mg)$^{1/n}$**	**1/n**	**R^2**
ME	40	0.23	0.98
CN	30	0.26	0.96
F400	53	0.22	0.99
IR	37	0.22	0.96
GT	22	0.30	0.92

4.2.3. Catalytic performance of the commercial carbons in the TBR system.

Phenol conversion evolution over time on stream for the TBR tests using these commercial AC is displayed in Figure 4.2.2. An inspection to Figure 4.2.2 shows that ME gave the highest phenol conversion at steady state, around 45%. The corresponding phenol conversion achieved for IR, F400 and CN are between 20, 36 and 32%, approximately. It must be noted that GT rendered practically negligible catalytic activity for CWAO. These differences hardly can be ascribed to the textural properties or the surface chemistry. As it can be seen in Tables 4.2.1 and 4.2.2, all the samples have very similar textural properties, and there are no considerable differences regarding to the chemical characteristics, i.e. surface oxygen groups.

Neither, the phenol adsorption capacity appears to be correlated with the phenol conversion achievable, since all they provide good adsorption capacities. As stated, Figure 4.2.1 makes evident that the adsorption capacity of all these carbons is really similar, being the highest difference, between F400 and ME, of only 30%, 340 mg/g AC and 262 mg/g AC, respectively. However, ME giving the best phenol conversion is not the activated carbon with the highest phenol adsorption capacity. The lack of correlation is even more manifest when GT is concerned it yields negligible conversion although its adsorption capacity is of the same order.

Adsorption capacity no even completely governs the transition period after start-up, i.e more or less during the first 10 hours of operation in the TBR. In this period, the apparent 100% phenol conversion is due to the adsorption that takes place on AC simultaneously with the oxidation reactions. Obviously, not all the commercial activated carbons behave the same way. Figure 4.2.2 evidences that only ME is capable of completely removing phenol from the effluent after 6 hours of operation, i.e. the activated carbon bed has not been yet equilibrated. By hour 10, all carbons except ME, were already equilibrated, so that this compound starts to appear in the exited effluent. Assuming that the activated carbon equilibrates with a 5000 mg/L phenol solution (which is not actually true as the simultaneous disappearance of phenol by oxidation results in a decreasing phenol concentration profile inside the reactor) the time needed to saturate the AC can be estimated taking into account the feed flow rate and the mass of the activated carbon bed If so, ME retained phenol for a longer time that that predicted, which indicates that many phenol is destroyed meanwhile. The opposite behaviour can be observed for GT. According to its adsorption capacity, which is similar to ME, GT should be saturated after 8 hours of operation, but after just 4 hours it becomes incapable of retaining more phenol. Since GT provides nil destruction of phenol, this indicates kinetic limitations for adsorption in a bed, so probably the microporosity is not fully used for adsorption. In conclusion the adsorption capacities could not be related with the catalytic activity.

The main distinction between all the five samples lies at the iron content. It can be seen that, activated carbons giving significant phenol conversion have a remarkable iron content. However, there is not direct correlation between the iron content and the phenol conversion. For instance, ME and CN, practically have the same iron content (0.4%wt), but the final conversions at steady state are different one from each other, 45% and 30% respectively. Concerning to F400, which has the half the iron content than ME, gave a conversion of 38% at steady state. In turn, IR has the same iron content than F400, but a lower conversion was obtained, only 17%. Irrespective of the different phenol conversion achieved, this suggests that only if iron is present in the activated carbon, it is able to effectively perform as catalyst for wet oxidation. It is known that the mineral matter of the carbon is constituted mainly by inorganic salts of a diversity of metals, among them iron. However, the different behaviour also indicates that the location and/or the state of the iron play a key role in its performance.

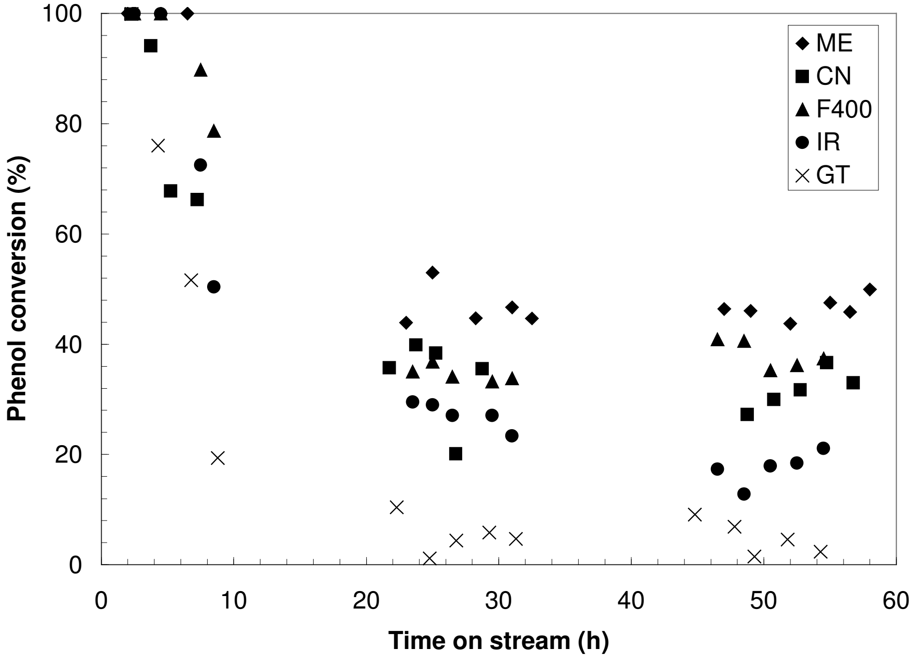


Figure 4.2.2. Phenol conversion in TBR reactor using commercial activated carbons, at 140ºC and 2 bar of oxygen partial pressure.

A wide literature dealing with iron fixed on zeolites has proven that the position of the iron in the frame of the zeolites is determinant for the type of product obtained in applications of these materials as catalyst for the oxidation of phenol in aqueous phase. Phu et al. (2001) observed that extra-framework Fe can catalyse the oxidation of phenol more selectively into CO_2 than the extra-framework Fe. Iron molecules in the AC's could be located deeply embedded in the carbonaceous matrix, or more superficially forming salts. Therefore, different iron location in the carbonaceous structure could explain the disparity in catalytic activity of the commercial carbons studied in this section, assuming that iron is responsible for the catalytic behaviour.

In all the cases, the ΔW at the end of the test was positive (Table 4.2.4), being the gain for GT the highest value. As GT is not able to oxidise phenol, oxidative coupling dominates and the extent of the formation of phenolic condensation products, which later remains attached to the activated carbon surface, is larger. This carbon also furnishes the higher pH in the exited liquid effluent, 3.65. This clearly is related to the low catalytic activity shown by GT. Since the acidity of the liquid stream is directly related with the amount of acid intermediates produced from the phenol oxidation, the low phenol conversion yields higher pH.

Table 4.2.4. Weight difference in commercial AC's samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
ME	2.519	2.13
CN	2.119	2.78
F400	2.496	2.18
IR	2.387	2.41
GT	2.829	3.65

Differences between phenol and TOC conversions obtained with these commercial carbons are very similar, 13%, 15% and 18% for samples ME, CN and F400, respectively (see Figure 4.2.3). The difference for IR is only 7%, which indicates a better selectivity towards CO_2. As described in section 4.1.2 for HD's carbons, despite the lower phenol conversion given by IR, the CO_2 selectivity is more favourable than those obtained from carbons exhibiting higher catalytic activity. Slightly negative differences calculated for GT could be explained by some possible desorption of phenolic polymeric compounds, which are not taken into account in the phenol quantification by HPLC, but that are indeed later measured in the TOC analysis increasing its value, therefore giving negative differences. Anyway, both phenol and TOC conversions for IR are very low and the difference fall into the range of experimental error.

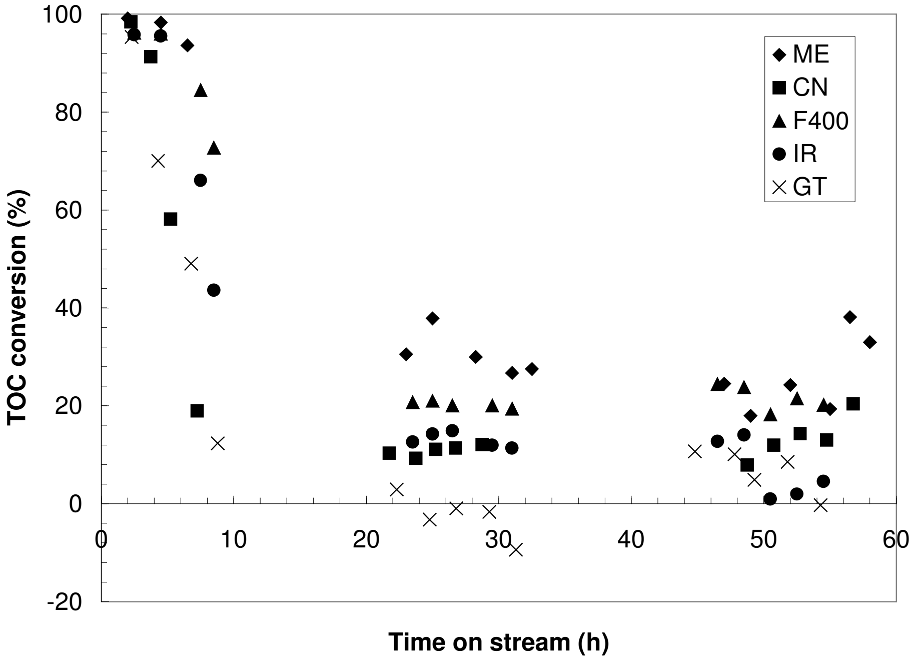


Figure 4.2.3. TOC conversion in TBR reactor using commercial activated carbons, at 140ºC and 2 bar of oxygen partial pressure.

Concerning to the distribution of intermediates, it must be noticed that the commercial carbons giving lower phenol conversion also render low yield in acid compounds. Partial oxidation products from phenol oxidation using GT as catalyst were acid compounds in a 25%, and 29% for IR. Samples CN and F400 achieved 69% and 85%, respectively, of acids, whereas the higher formation of acids was obtained for ME, 94%. In summary, these results indicate that the higher the phenol conversion, the larger the formation of acidic compounds, as generally expected from a reaction pathway based in consecutive reactions (Eftaxias et al., 2006).

4.3. Preliminary remarks

Based on the results from the experiments completed using the different activated carbons described in sections 4.1 and 4.2, it is possible to make several preliminary assertions.

As discussed in the introduction chapter, the porosity of the activated carbons is determinant when evaluating its adsorption capacity towards any compound. For phenol, due to its molecular size the adsorption takes place mainly in the micropores. Because of this, highly microporous carbons are expected to exhibit high phenol adsorption capacities. Carbons ME, CN, F400, IR, GT, WV1 and WV2, which have a great percentage of its porosity in the micropore range show good adsorption capacities towards phenol (see Figures 4.1.10, 4.1.22 and 4.2.1). Samples derived from HD, which are more mesoporous, have a lower adsorption capacity when compared to ME (see Figure 4.1.17). Acid surface groups decrease the phenol adsorption capacity due to the formation of water clusters that hamper the access to phenol molecules. Moreover, they impede the formation of electron donor-acceptor complexes, one of the mechanism responsible for phenol adsorption. Thermal treatment under N_2 or H_2 demonstrated to be effective in removing most of the oxygen surface groups without affecting textural properties, thus enhancing the phenol adsorption mechanisms and increasing the adsorption capacity in all cases (see Figures 4.1.10, 4.1.17 and 4.1.22). Nevertheless, there is no correlation between the phenol conversion in CWAO and the adsorption capacity of the activated carbon used as catalyst.

Neither, a relationship between textural properties or surface oxygen functional group content and type with the catalytic activity can hardly be established. For instance, thermal treatment over ME did not improve its catalytic behaviour. But the increase in the microporosity of sample HDD by steam treatment (HHDS) with a latter thermal treatment un hydrogen to eliminate oxygen from surface (HDDSH) increased the conversion obtained from 20% to 40%. On the other hand, high microporosity of WV1 and WV2 did not furnish noticeable catalytic activity, even after thermal treatment under hydrogen in order to eliminate surface acid groups. Also, highly microporous commercial carbons show very different values of phenol conversion (see Figure 4.2.2).

On the contrary, when considering the mineral content, specifically iron content, two facts must be noted. Samples WV1, WV2 and GT containing marginal iron content, because its raw material originally had no iron content, showed very poor catalytic activity, only 11% for WV2 or even lower, 5%, for GT. However, activated carbons made from coals, with iron content ranging from 0.03 to 0.4% wt, offered higher phenol conversions, from 20% for IR and HDDS up to 45% for ME.

Based on these facts, in the next sections, the results from experiments designed to evaluate the impact of the iron content and the mesopore volume on the catalytic activity of activated carbon are presented. Carbon ME was chosen as base carbon for the modifications proposed, due to its high surface area and micropore volume, high iron content and because the high phenol conversion naturally achieved with this carbon. First, the effect of acid wash, i.e. demineralisation, on the properties of ME is studied in section 4.4, whilst the modification of the iron content and the mesopore volume impact on the performance of ME as catalyst are evaluated in section 4.5.

4.4 Demineralisation of ME activated carbon

4.4.1. Physical and chemical characterisation

As previously mentioned, demineralisation by HCl solution was applied to significantly reduce the mineral matter. i.e. metal content, of the ME. For the demineralised ME, MED, only a slight decrease in the meso- and macropore volumes were observed as shown in Table 4.4.1, while surface area and micropore volume remain almost unaltered. On the contrary, after treatment with an oxidant acid as HNO_3, MEN1, the modification of textural properties was severe. The surface area decreases 66%, and the overall porosity about 68%.

Chemical properties of the acid wash ME samples are collected in Table 4.4.2. The iron content of the parent ME carbon was about 0.4% and no considerable amount of other metals was found on it. Demineralisation procedure decreases the iron content about 60%, while small change was observed in the overall surface acidity, as indicated from the pH_{pzc} value, although some carboxylic groups were generated , thus decreasing somewhat the pH_{pzc}.In contrast, treatment done with HNO_3 drastically decreases the pH_{pzc}, mainly due to the formation of apparently more carboxyls. The content of carboxylic groups increased in sample MEN1 by a factor of 45 with respect to the parent ME, whereas the increase in MED was just 3.5 times. However, it must be pointed out that treatment with HNO_3 also can result in the creation of nitrogen containing surface groups at some extent, and strongly adsorbed nitric acid, which imparts additional acid character to the material (Salame and Bandosz, 1999). As predicted, iron content was also affected by the acid wash, which was reduced a 60% by HCl treatment and a 70% by HNO_3 treatment. However, it must be noted that an even noticeable amount of remaining iron amount was present in both MED and MEN1 activated carbons, which is expected to provide significant catalytic activity for CWAO.

Table 4.4.1. Physical properties of parent and modified ME.

Sample	SA_{BET} (m^2/g)	V_{mic} D-R (cm^3/g)	$V_{mes+mac}$ (cm^3/g)	V_{tot} (cm^3/g)
ME	1261	0.473	0.137	0.610
MED	1272	0.484	0.108	0.592
MEDH	1275	0.490	0.195	0.685
MEN1	430	0.176	0.020	0.196

Table 4.4.2. Chemical properties of parent and modified ME.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH_{pzc}	Fe content (%wt)
ME	0.097	0.123	0.031	7.36	0.40
MED	0.010	0.117	0.113	6.90	0.16
MEDH	0.061	0.000	0.000	10.33	n.m.[a]
MEN1	0.019	0.068	1.393	3.02	0.12

[a] It is expected that iron content of MEDH is about that of MED, i.e., 0.16%.

4.4.2. Adsorption isotherms.

The results displayed in Figure 4.4.1 show that demineralisation increased the phenol uptake 20% for MED, probably due to a reduction in the overall surface polarity and hydrophilicity. As previously mentioned, the mineral content of the MED was below half of that present in ME, although the overall concentration of oxygen containing groups was similar. By demineralisation and the subsequent elimination of metal-oxygen complexes that could be located at the edges of the carbon pores, phenol adsorption is enhanced because of the higher hydrophobicity also avoiding the formation of water clusters as already mentioned several times. However, there is no important modification on the adsorption capacity of MED after hydrogen treatment. Instead, nitric acid wash, MEN1, strongly decreases the adsorption capacity of ME down to 148 mg/g AC, 45% lower than that of the parent ME, 262 mg/g AC. This worsening could be attributed to the evident loss of microporosity and surface area, and to the much higher content of acidic groups on MEN1 surface.

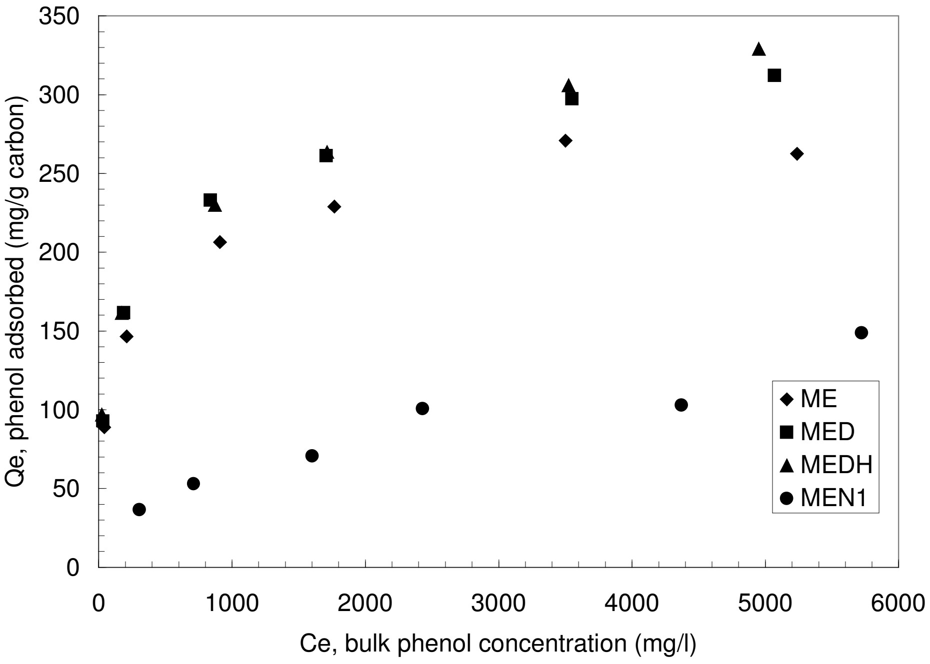


Figure 4.4.1. Phenol adsorption isotherms over activated carbon at 20ºC.

The low 1/n values of Freundlich parameters shown in Table 4.4.3 indicates that the adsorption is still favoured by good interactions between phenol and the carbon surface. In sample MEN1, this value increases to 0.45, indicating that in this case the adsorption capacity was clearly less favourable after modification by HNO_3 wash.

Table 4.4.3. Freundlich parameters for phenol adsorption of the demineralised ME's set of carbons.

Sample	K (mg/g AC)(l/mg)$^{1/n}$	1/n	R^2
ME	40	0.23	0.98
MED	43	0.24	0.98
MEDH	49	0.23	0.99
MEN1	3	0.45	0.96

4.4.3. Catalytic performance of carbons in the TBR system.

Figure 4.4.3 depicts the phenol conversion profiles for the different demineralised samples. It can be seen that demineralisation causes a considerable reduction in the phenol conversion. This value decreases from 45% for the parent ME down to 25% for the demineralised carbons, regardless the treatment applied. Micropore volumes of all carbons are similar (in the case of MED is even higher), therefore it cannot be the reason for the different phenol conversion. On the other hand, the slightly lower overall porosity of MED (only 3% lower) contrasts with the much lower porosity of MEN1, but both gave a lower phenol conversion. Neither, stabilisation by hydrogen treatment and an almost complete elimination of oxygen containing groups, MEDH, prevents this demineralised sample from rendering worse phenol conversion. The lower adsorption capacity of sample MEN1 clearly affects the adsorption controlling initial period of reaction, i.e. first hours of operation, as phenol was detected in the outlet effluent just two hours after start-up. Nonetheless, this lower adsorption capacity has no impact on the phenol conversion at steady state, thus being comparable to the rest of the demineralised samples. Therefore it can be concluded that the catalytic activity shown by ME carbon must indeed be ascribed to the iron present on its mineral matter.

Difference between phenol and TOC conversions, the latter presented in Figure 4.4.4, is about 5% for samples MED and MEDH. In this case, the thermal treatment under hydrogen did not modify the selectivity towards CO_2 as discussed in the subsection 4.1.1 where the effect of hydrogen thermal treatment on carbon ME was discussed. In any case, some detrimental effect was observed for carbon MED, since the difference of conversions is 13%, which means a lower selectivity towards CO_2.

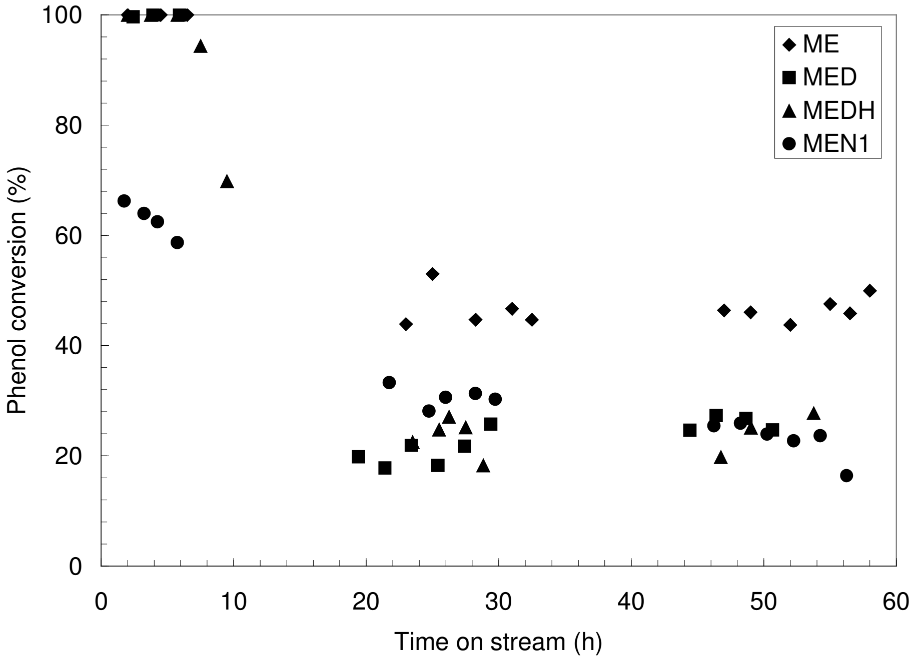


Figure 4.4.2. Phenol conversion in TBR reactor using ME and acid wash modified samples, at 140ºC and 2 bar of oxygen partial pressure.

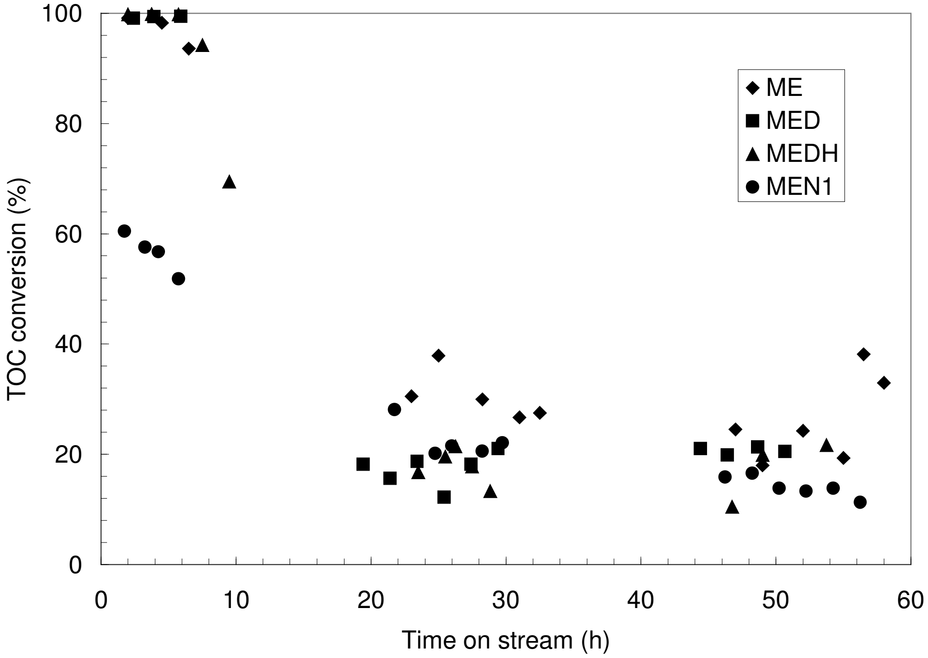


Figure 4.4.3. TOC conversion in TBR reactor using ME and acid wash modified samples, at 140ºC and 2 bar of oxygen partial pressure.

All samples except MEN1 have similar ΔW after 55 hours of operation inside the reactor. In all the cases, the weight increased, which indicated that phenolic chains were irreversible adsorbed onto the activated carbon after operation. It must be noticed that ME, MED and MEDH show similar behaviour, whilst the lower value observed for MEN1 could be related to the initial presence of more carboxylic surface groups, which prevent the formation of phenol condensation compounds by oxidative coupling as previously commented.

Table 4.4.4. Weight difference in ME and acid wash modified samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
ME	2.519	2.13
MED	2.496	2.35
MEDH	2.400	2.49
MEN1	1.067	2.33

4.5. Metal impregnation of ME activated carbons

4.5.1. Physical and chemical characterisation

In this section, the results obtained for a set of activated carbons derived from the parent ME are presented. The ME activated carbon was subjected to different procedures in order to enhance its mesoporosity and then to deposit iron by impregnation. First, acid treatment with HNO_3 or H_2SO_4 was carried out with the double objective of demineralising and mainly generating acid sites for enhanced iron impregnation.

Table 4.5.1 shows that the acid treatment did not significantly modify the surface area and micropore volume of ME, as seen for samples MES and MES. However, an important increase of the mesopore volume can be observed, mainly in the sample washed with H_2SO_4, which increased three folds, while HNO_3 only doubles the micropore volume. After impregnation with iron or calcium and subsequent carbonisation at 1000ºC, the mesopore volume was even enhanced, but the other textural properties did not undergo major changes. The mesopore volume was at least increased by a factor of 2.5 for all the impregnated samples. It must be pointed out that the mesopore volume enlarges up to 0.108 cm^3/g for MESCa. There are evidences that sulphuric acid widens the existing porosity of activated carbons (Jiang et al., 2003). Also, calcium has been used before as a promoter of mesoporosity in the production of activated carbon from sewage sludge (Rio et al., 2005a). It has been proposed (Zheng and Kozinski, 2000) that above 800ºC calcium carbonate decomposes releasing CaO and CO_2. The release of CO_2 can enlarge the existing pores but can even form new pores. Since all samples were heated at 1000ºC, the calcium carbonate decomposition can explain the increase in the porosity of all samples containing Ca. In fact, MESCa owns the highest overall pore volume (0.631 cm^3/g). In this case, the two effects, i.e. sulphuric acid wash and $CaCO_3$ decomposition, contributed to the observed increase. In all the samples impregnated with iron, an increase in the mesopore volume can also be generally observed, yet it is more moderate. This can be explained by the catalytic effect of iron in the carbonisation of activated carbon also releasing CO_2, with the same enlarging pore effect already described. The microporosity of all samples remain practically unchanged, .although generally a slight decrease can be noted. The highest decrease was observed for MENCaFe being about 13%. However, the loss of total pore volume in that sample is just 5%, keeping practically the total volume from the parent ME, yet that with a different distribution. In general, all samples are still highly microporous, since the micropore volume means around 80% of the total porosity.

Table 4.5.1. Physical properties of parent and modified ME.

Sample	**SA_{BET} (m^2/g)**	**V_{mic} (cm^3/g)**	**V_{mes} (cm^3/g)**	**V_{tot} (cm^3/g)**
ME	1206	0.483	0.029	0.569
MEN	1149	0.459	0.068	0.577
MES	1261	0.499	0.092	0.653
MEFe	1119	0.448	0.072	0.567
MENFe	1085	0.431	0.082	0.562
MESFe	1147	0.453	0.087	0.599
MECa	1111	0.444	0.074	0.566
MENCa	1117	0.442	0.075	0.573
MESCa	1175	0.461	0.108	0.631
MECaFe	1126	0.451	0.072	0.572
MENCaFe	1052	0.417	0.072	0.541
MESCaFe	1158	0.456	0.085	0.608

Table 4.5.2 proves that the carbonisation step at 1000ºC under N_2 was effective for removing carboxylic and phenolic groups from surfaces of samples MEFe, MECa and MECaFe. However, it is noteworthy that samples that were acid treated show an increase in the carboxyl and lactone content. This latter apparently increased over four times for MESCa. A total elimination of phenolics was nearly achieved in all cases. An explanation for these results could be that some residual sulphuric or nitric acid could remain trapped in the pores, thus reacting with the bases used in the Boehm titrations, resulting in a higher consumption and false surface oxygen content, higher than that actual. Also, iron imparts acid character and contributes to the acidity of the carbon.

Table 4.5.2. Chemical properties of parent and modified ME.

Sample	**Phenolics (meq/g)**	**Lactones (meq/g)**	**Carboxyls (meq/g)**	**pH_{pzc}**
ME	0.097	0.123	0.031	7.36
MEFe	0.033	0.075	0.000	8.55
MENFe	0.119	0.202	0.049	7.99
MESFe	0.021	0.074	0.048	8.27
MECa	0.000	0.128	0.000	8.84
MENCa	0.002	0.142	0.035	9.36
MESCa	0.000	0.531	0.011	10.77
MECaFe	0.000	0.359	0.000	8.57
MENCaFe	0.000	0.441	0.006	8.63
MESCaFe	0.000	0.352	0.030	7.66

In Table 4.5.3, Fe and Ca content of all samples is collected. In general terms, acid wash was an effective pre-treatment for creating groups with ion-exchange ability, since the higher metal contents are found for the samples previously washed with acid, particularly those treated with H_2SO_4. The increase of metal content, yet rather small, in sample ME not treated with acid, MEFe could be explained by the originally already notable amount of surface oxygen groups that this activated carbon exhibits. Obviously, the creation of new ion-exchange sites by acid wash promotes an increase in the amount of metal that is later fixed in the carbonaceous structure during the carbonisation. Combined metal impregnation was effective, because the content of both metals increases in all the cases. However, the amount of calcium impregnated in these combined samples was lower than when using single calcium impregnation. This could be explained by the fact that calcium carboxylates formed on ME surface undergo dissociation, releasing calcium ions thus lowering the content fixed if compared with the sample only impregnated with calcium acetate. These carboxylic groups releasing calcium ions can later fix iron. This explains why MECaFe gave a higher iron content than MEFe, specially when considering that none of them were treated with acid. MENCaFe showed the same calcium content than MECaFe, but the iron content is practically two times higher, this suggests that the carboxylic groups created by the acid wash help the fixation of iron rather than calcium. MESCaFe showed a slight increase in calcium content compared to MECaFe and MENCaFe, but lower iron content than MENCaFe, which indicates that H_2SO_4 is not so suitable for fixing iron.

Table 4.5.3. Iron and calcium content of ME and modified samples.

Sample	**Fe content (wt%)**	**Ca content (wt%)**
ME	0.40	0.15
MEFe	0.51	n.m.
MENFe	1.43	n.m.
MESFe	2.08	n.m.
MECa	n.m.	0.40
MENCa	n.m.	0.79
MESCa	n.m.	0.90
MECaFe	0.75	0.20
MENCaFe	1.88	0.30
MESCaFe	1.15	0.20

n.m. Not measured

4.5.2. Adsorption isotherms.

Figure 4.5.1 shows the phenol adsorption isotherms for all these samples. In general, all samples impregnated with either Fe, Ca or both exhibit higher adsorption capacity than the parent ME. Also, MESCa shows a high adsorption capacity compared to the other Ca impregnated samples. This could be related to the high mesopore volume of this sample, which allows adsorbing a higher amount of phenol. An increase in the adsorption capacity in all samples was indeed expected, since it is well known that elimination of oxygen functionalities favours the adsorption of phenol on the activated carbon surface. In the case of samples that were impregnated with both metals, the adsorption capacity increases a quite high 58%, approximately.

Parameters of Freundlich equation for the adsorption isotherms are given in Table 4.5.4. In general terms, all samples have a low value of the 1/n parameter, again indicating favourable phenol-AC surface interactions. Also, all R^2 values are higher than 0.97, which means that all isotherms fit very well the model.

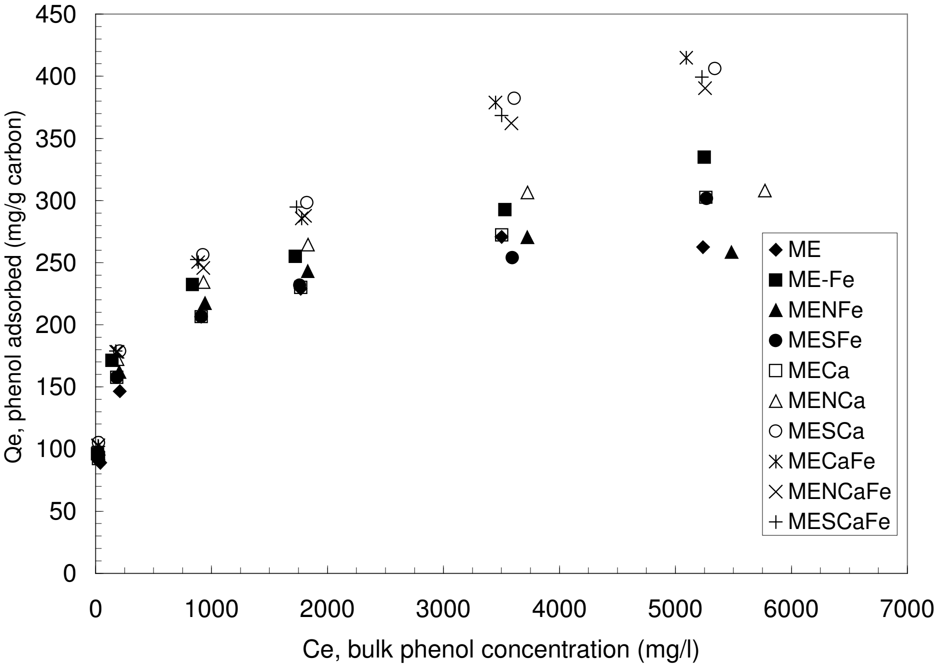


Figure 4.5.1. Phenol adsorption isotherms over activated carbon at 20ºC.

Table 4.5.4. Freundlich parameters for phenol adsorption on ME and metal impregnated samples.

Sample	K (mg/g AC)(l/mg)$^{1/n}$	1/n	R^2
ME	40	0.23	0.98
MEFe	55	0.21	0.98
MENFe	56	0.19	0.97
MESFe	52	0.20	0.99
MECa	48	0.21	0.99
MENCa	54	0.21	0.98
MESCa	45	0.26	0.99
MECaFe	47	0.25	0.99
MENCaFe	47	0.24	0.99
MESCaFe	47	0.25	0.99

4.5.3. Catalytic performance of carbons in the TBR system.

Regarding the catalytic activity, the phenol oxidation conversions as a function of time obtained in the TBR tests are represented in Figure 4.5.2. Considering the catalytic performance, two different behaviours can be distinguished Samples with similar or lower catalytic activity than ME (MECa, MECaFe, MENCa, MESCa), , and samples giving considerable higher conversion (MENFe, MESFe, MENCaFe, MESCaFe). MEFe shows intermediate trends. The results demonstrate that the addition of iron largely enhances the catalytic behaviour of the activated carbon. Thus, samples containing Fe, i.e. MENFe, MESFe, MENCaFe and MESCaFe render steady conversion around 75%, well above the 45% given by the parent ME. Sample MEFe, which has just 0.1% wt more Fe content than the parent ME shows an intermediate increase of 15% of conversion, demonstrating that even a small increase in the amount of iron available in the carbon could improve the catalytic performance.

The incorporation of calcium to the carbon did not modify the catalytic activity, since samples MECa, MENCa and MESCa did not furnish better performance than the parent ME. However, it must be noted that both MENCa and MESCa are acid washed samples, so that the actual iron content is expected to be lower. Therefore, the predicted phenol conversion should be poorer. Instead, the obtained conversion is comparable to that of the parent ME. This unexpected trend could be ascribed to the higher mesopore volume of these samples, which suggests that mesoporosity also plays a relevant role.

Albeit it must be also pointed out that MECa, which is not acid washed, should give better phenol conversion than that found, as it should contain the original Fe content but with enhanced mesoporosity. A possible explanation might relate this fact to the presence of Ca; iron could be hindered by calcium hydrated ions, then making original iron less available. In turn, MECaFe is not affected by this drawback as Fe was impregnated after Ca.

Due to the typically acidic reaction conditions in the TBR, leaching of iron (also Ca) is likely and therefore it was measured. Values of metal content at the end of the CWAO runs are collected in Table 4.5.6. It must be clarified that the metal content calculations of the spent carbons were done using the mass obtained after use. This mass includes also the products of the oxidative coupling occurring inside the reactor. This last value was used since it is difficult to ascertain the actual amount of the remaining activated carbon, since the possible loss of carbon mass could be largely offset by the increase due to the attached polymeric material. Figures 4.5.3, 4.5.4 and 4.5.5 compared the metal content before and after use. Regarding Ca, the leaching in samples MENCa and MESCa was about 70% in both cases. This means that, after 55 hours on stream, the Ca content was very close to that original. A different trend is found for Fe. Samples MENFe and MESFe show leaching of 15% and 53%, respectively, which clearly indicates that nitric acid wash before impregnation was more effective in order to incorporate iron to the activated carbon. However, even in the case of MESFe, which lost half of its initial iron content after 55 hours on stream. Anyway the final value is still threefold in comparison to that of the parent ME, allowing the phenol conversion to reach a value 30% above that given by the parent ME. Samples containing both Fe and Ca present high leaching of both metals, over 85% percent in all cases except for iron in sample MECaFe, which is only 47%.

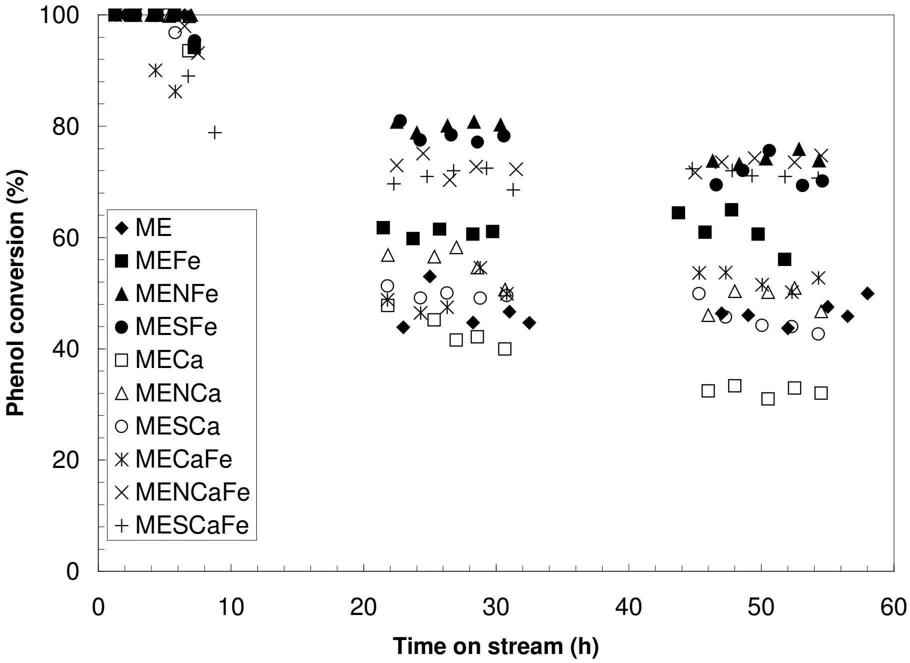


Figure 4.5.2. Phenol conversion in TBR reactor using ME and metal impregnated modified samples, at 140ºC and 2 bar of oxygen partial pressure.

Table 4.5.5. Fe and Ca content after used in CWAO

Sample	Fe content (% wt)	Ca content (% wt)
ME	0.31	0.02
MEFe	0.61	n.m.
MENFe	1.22	n.m.
MESFe	0.98	n.m.
MECa	n.m.	0.33
MENCa	n.m.	0.23
MESCa	n.m.	0.27
MECaFe	0.40	0.02
MENCaFe	0.21	0.03
MESCaFe	0.17	0.02

n.m. Not measured

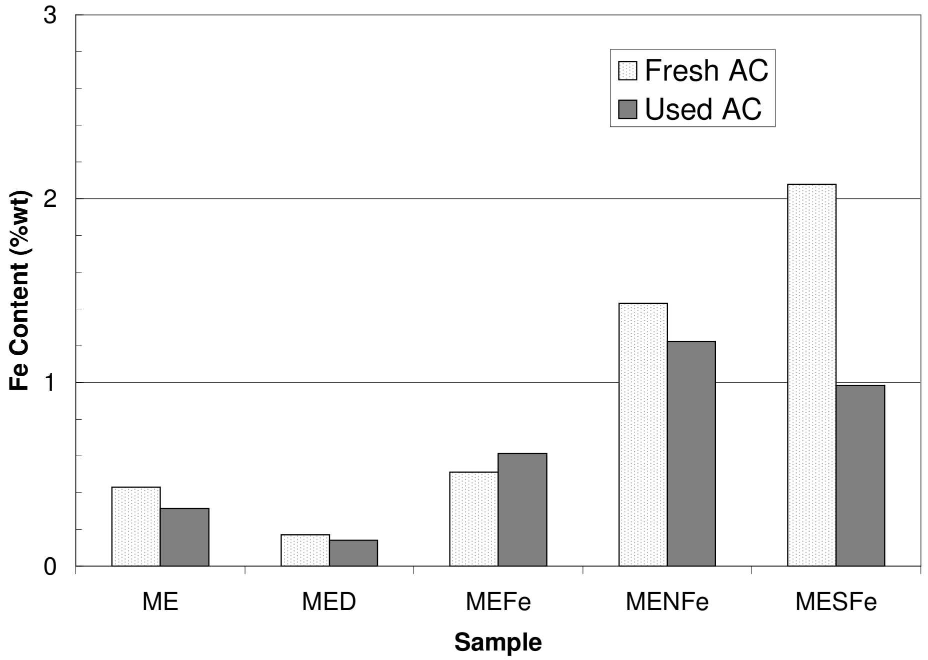


Figure 4.5.3. Iron content expressed in %wt of fresh and used in CWAO activated carbons.

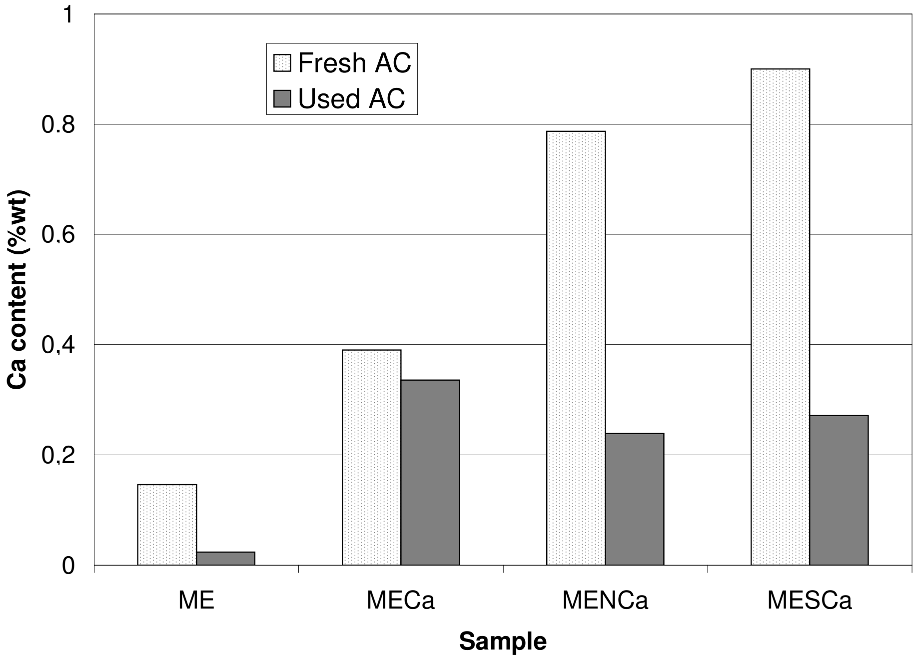


Figure 4.5.4. Calcium content expressed in %wt of fresh and used in CWAO activated carbons.

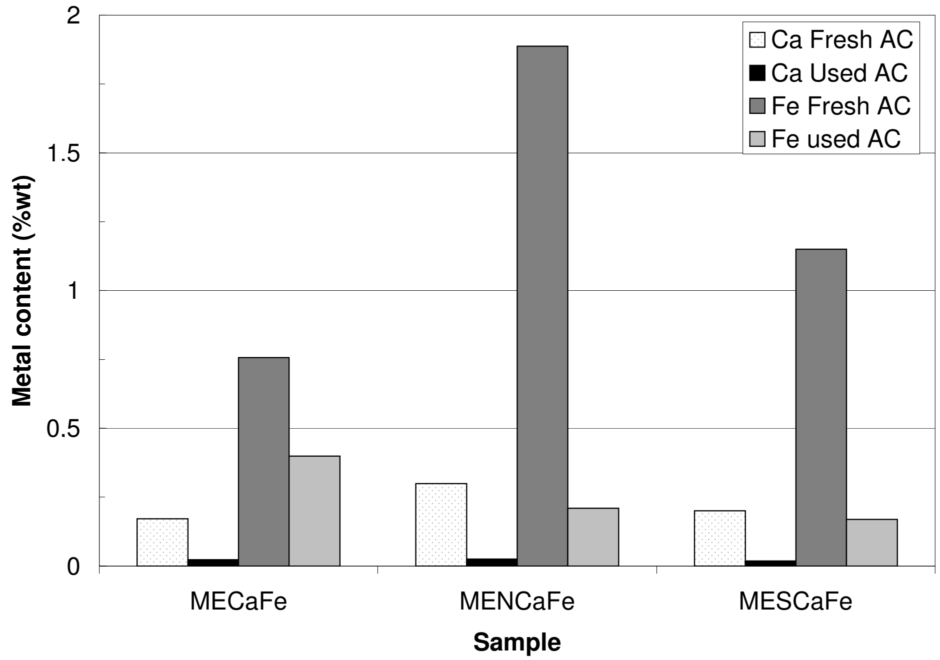


Figure 4.5.5. Iron and calcium content expressed in %wt of fresh and used in CWAO activated carbons.

TOC conversion in the effluent exiting the reactor during the run was measured and the results are presented in Figure 4.5.6. TOC behaviour shows similar trends than phenol conversion. Overall, the incorporation of iron improves the TOC conversion achieved at steady state. As before seen for phenol conversion, the presence of calcium and its derived enhanced mesopore volume did not improve the performance of MECa, MENCa or MESCa in comparison to ME.

Probably because of the leaching and the presence of iron in the liquid stream (Table 4.5.7), the different TOC conversion obtained with samples MENFe, MESFe, MENCaFe and MESCaFe, unlike what was observed for phenol conversion, where all these samples gave similar values, could be explained. These results suggest that homogeneous iron is promoting further degradation of the phenol partial oxidation products, e.g. quinone like compounds, carboxylic and condensation products.

Table 4.5.7 also summarises the weight of the activated carbon bed after use. All samples showed increase in the final weight, which reveals deposition of phenolic polymeric compounds as a product of the oxidative coupling occurring over the activated carbon.

In addition, all samples impregnated with iron showed an important fraction of the intermediates as acidic compounds, which agrees with the low pH values encountered in the exited effluent, also collected in Table 4.5.7. The amount of acid compounds was higher than 85% of the total partial oxidation compounds for all cases. This value is lower than the 94% obtained with ME, but it is important to highlight that both phenol and TOC conversions also increased for all the activated carbons impregnated with iron, except MECaFe, which gave approximately the same conversion than ME. Therefore, even being lower the acid content, the performance of Fe impregnated carbons is more favourable as the phenol conversion is significantly higher.

A further inspection to Table 4.5.7 illustrates that the high values of Fe in the aqueous phase, because of the leaching, coincides with those cases achieving high phenol conversion. Therefore, it was mandatory to determine whether or not the phenol conversion reached was resulting from the iron impregnated over the activated carbon, or the homogeneous iron could be contributing to phenol disappearance.

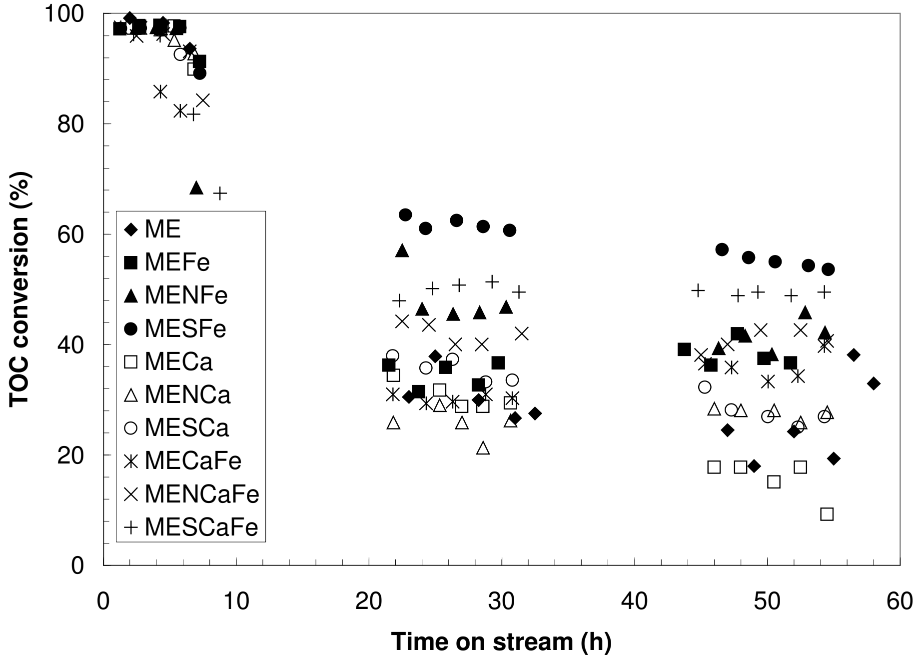


Figure 4.5.6. TOC conversion in TBR reactor using ME and metal impregnated modified samples, at 140ºC and 2 bar of oxygen partial pressure.

Table 4.5.6. Weight difference in ME and acid wash modified samples after operation in TBR, final pH and iron content of liquid stream.

Sample	ΔW (g)	Final pH on stream	Fe in aqueous phase (mg/L)
ME	2.519	2.13	9.9
MEFe	2.407	2.41	13.5
MENFe	2.000	2.29	14.7
MESFe	1.687	2.27	19.6
MECa	2.466	2.50	0.5
MENCa	2.283	2.43	1.5
MESCa	2.126	2.34	0.5
MECaFe	2.592	2.33	5.5
MENCaFe	2.081	2.13	25.3
MESCaFe	1.866	2.39	17

Figure 4.5.7 assesses the phenol conversion obtained from several tests carried out with iron in homogeneous phase, using ME to fill the reactor and carborundum, which is an inert material. Using ME to fill the reactor and adding iron in the feed solution, 20 mg/L, no improvement in the final conversion is observed (test MEFeHom). Actually the conversion after 50 hours of run is even 10% lower than that obtained with ME (45%). Adding iron in the feed solution using silicon carbide as bed (test InFeHom) barely reached a 10% of conversion. Although homogeneous Fe indeed provides some catalysis, this is not high enough as to explain the improved performance of the iron impregnated samples. Therefore, the enhanced catalytic performance must be mostly ascribed to the Fe supported over the modified activated carbons.

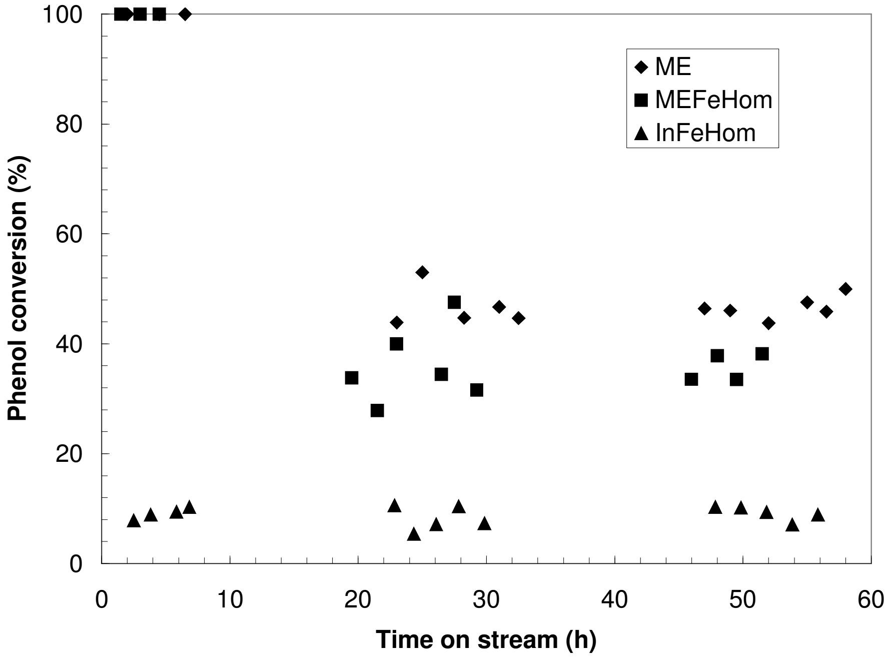


Figure 4.5.7. Phenol conversion in TBR reactor using ME and homogeneous iron, at 140ºC and 2 bar of oxygen partial pressure.

4.6 Additional remarks

From results presented in subsections 4.4 and 4.5, it is possible to state that iron contained in ME is determinant in the catalytic activity shown by this commercial carbon for CWAO of phenol. The improvement of the mesopore volume, e.g. MECa (Table 4.5.1), did not modify the catalytic behaviour since the phenol conversion was practically the same than that obtained with the parent ME. Activated carbons impregnated with iron give much better catalytic performance that the parent ME. This additional catalytic activity can be ascribed to the impregnated iron, even occurring some iron leaching, as homogeneous iron cannot provide the additional phenol conversion encountered. Therefore, it is proposed that iron content is the main parameter responsible for the catalytic activity of activated carbon, which agrees with the known catalytic properties of this metal.

Because of this, the tailored manufactured activated carbons were intended to reproduce these conditions by means of designed experimental procedures.

4.7. Designed activated carbons

4.7.1. Physical and chemical characterisation

This part of the research work was developed at the laboratories of the Centre for Environmental Control and Waste Management (CECWM) of the Imperial College of London. The raw material for preparing the activated carbons were supplied by the laboratory and the temperature and time selected for the manufacturing of activated carbon from willow had been already optimised in a previous research owned by CECWM. The one-step pyrolysis procedure was chosen in order to obtain activated carbons comparable to the parent ME. This method allows making the carbonisation and activation of the raw material in practically just one single step. Steam chosen as activation agent since was selected because it promotes the development of microporosity during the activation stage (Ioannidou and Zabaniotou, 2007).

Table 4.7.1 summarises the liquid and solid products rendered during the manufacture of the activated carbons. Sample MW1, made from willow through one-step pyrolysis, gave higher liquid yield than when the same raw material was used but chemical activation applied, in sample MW2, where the highest yield was gaseous products, specially for MW2Fe. This is due to the catalysing effect that metals like potassium and iron have on the gasification reactions during the activation. In fact, gas formation during the manufacturing of MW2Fe gave the highest gas yield observed in all cases. Iron in this case is accelerating the formation of CO and CO_2, decreasing also the solid yield if compared with MW2 that was made from the same raw material through chemical activation but without previous iron impregnation. The liquid product yield in sample MCS, made from coconut shells and by one-step pyrolysis activation, was very similar to that obtained with sample MW2. However, this value for MCSFe was the lowest of all the carbon manufactured because the carbonisation was conducted before the iron impregnation step, and the values in Table 4.7.1 are calculated from products obtained after the activation. In the manufacturing of the chars that were later used in the iron impregnation, the liquid products yield was about 70%. For that reason, after the iron impregnation and the activation with steam, the liquid product yield was only about 10%, because most of the organic material that is later released as oils was already eliminated in the char production step.

However, due to the nature of its raw material, the activated carbons MW1, MW2 and MW2Fe did not have the strengthness needed to withstand the exigent operation conditions in the TBR. For that reason, only carbons MCS and MCSFe made from coconut shells were employed in the performance tests of phenol adsorption and catalytic activity.

Table 4.7.1. Yields obtained in the manufacturing of activated carbons.

Sample	**Solid product (% wt)**	**Liquid product (% wt)**	**Gas + losses (% wt)**
MW1	17.1	51.7	31.2
MW2	14.9	38.8	46.3
MW2Fe	11.8	16.5	71.7
MCS	19.0	35.4	45.6
MCSFe	56.4	10.4	33.2

The physical properties of samples MCS and MCSFe are listed in Table 4.7.2. ME has been included for comparative purposes. MCS is a highly microporous carbon since 96% of its total porosity is in the micropore range. The surface area is also relatively high, which indicates that steam was effective as activating agent promoting the formation of micropores. Sample MCSFe, on the contrary, showed a surface area 40% lower than MCS and also 47% lower micropore volume. Despite the iron is supposed to enhance the gasification of the carbon, thus promoting the porosity, in this case the iron impregnated on the char made from the coconut shells could have reduced the interaction of the water with char and their needed reaction. As a result, development of the surface area and microporosity were suppressed and only superficial reactions, typically producing mesoporosity, promoted. Actually, some increase in the mesopore volume, from 4% to 9%, was observed in sample MCSFe (Marsh and Rodríguez-Reinoso, 2006; Alcañiz-Monge et al., 2007).

Table 4.7.2. Physical properties of tailored activated carbons.

Sample	**SA_{BET} (m^2/g)**	**V_{mic} D-R (cm^3/g)**	**$V_{mes+mac}$ (cm^3/g)**	**V_{tot} (cm^3/g)**
ME	1261	0.473	0.137	0.610
MCS	830	0.369	0.014	0.383
MCSFe	493	0.194	0.020	0.214

The nitrogen adsorption isotherms are shown in Figure 4.7.1. The shape of the isotherms for both activated carbons matches the Type I classification according to IUPAC, typical from highly microporous materials. The low adsorption capacity shown by MCSFe evidences the low value of surface area of this sample.

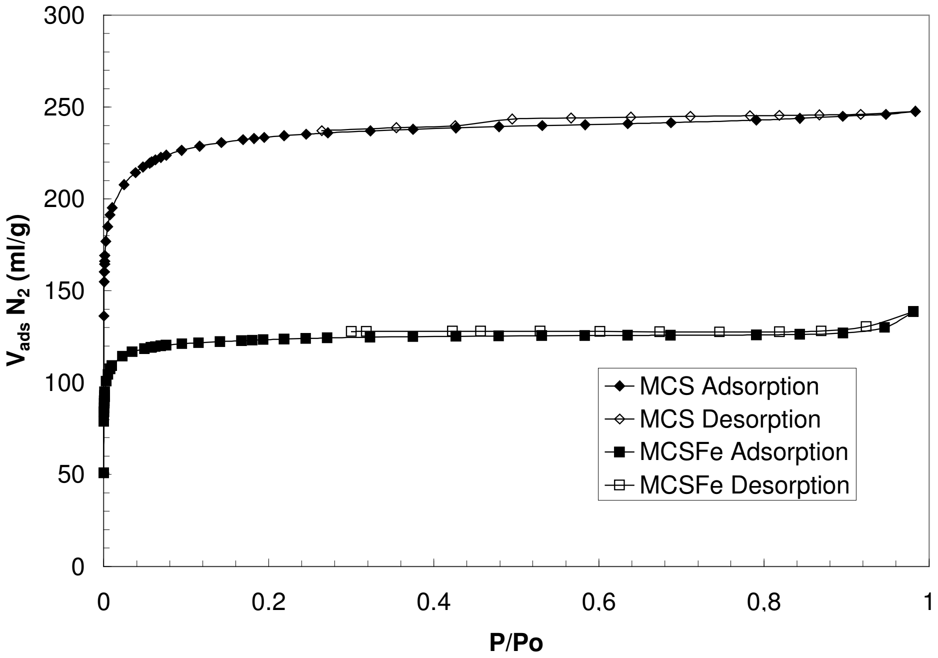


Figure 4.7.1. N_2 adsorption isotherms on tailored carbons.

Since one of the commercial carbons, GT, is also made from coconut shells, it was subjected to HNO_3 wash as previous pre-treatment to the iron impregnation later performed according to the procedure described in section 3.5. This sample, GTNFe, was prepared in order to compare the properties of the tailored activated carbon made from the same raw material and the adapted procedure.

Chemical properties of all samples are collected in Table 4.7.3. Samples MCS, MCSFe, MW1 and MW2 showed very high values of pH_{pzc}. This could be due to the elevated temperatures used for the activation step. Since, after the activation, the samples were left to freely cool from 1000ºC until room temperature under just the nitrogen flow, most of the acidic surface functionalities were probably decomposed in CO and CO_2 during cooling. Samples with iron content showed a more acidic character. In case of sample GTNFe, the previous HNO_3 wash could be imparting acidic properties to this sample as some nitric acid trapped into the pores in hard to remove. Also, the iron content contributes to the acidity of the carbons this could explain the low value showed by carbon MW2Fe.

In all the home-made manufactured activated carbons, the iron impregnation method was effective for fixing iron in the carbonaceous matrix, specially in MW2Fe. Anyway, iron content is very low probably because the impregnation was directly performed over the raw material without any previous pre-treatment, so that probably there was no acidic oxygen surface groups with ion-exchange ability. Therefore, the iron content was resulting from just physical adsorption of iron salts and then a low content must be expected.

Table 4.7.3. Chemical properties of tailored activated carbons.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH_{pzc}	Fe content (%wt)
ME	0.097	0.123	0.031	7.36	0.40
MCS	0.059	0.033	0.000	10.82	0.00
MCSFe	0.017	0.042	0.000	10.52	0.20
GT	0.000	0.021	0.193	9.19	0.00
GTNFe	0.093	0.313	0.026	6.92	0.30
MW1	0.069	0.063	0.000	11.82	0.00
MW2	0.087	0.041	0.003	11.63	0.00
MW2Fe	0.009	0.298	0.057	7.54	0.02

4.7.2. Adsorption isotherms.

The phenol adsorption isotherms of the tailored carbons are presented in Figure 4.7.2. Samples MCS and GT showed high adsorption capacity at 5000 mg/L of bulk concentration, in the same order of the parent ME. On the other hand, sample GTNFe showed a decrease of about 15% in its original adsorption capacity. The higher amount of oxygen surface groups present on this carbon and the presence of iron impart additional hydrophilic character to the carbon surface, which could be responsible for the reduction of the phenol adsorption capacity. As already commented, they could be promoting the formation of water clusters surrounding oxygen containing groups in the carbon surface However, the strongest phenol adsorption capacity reduction belongs to MCSFe giving loss of 74% in its original adsorption capacity. All carbons studied in this research have demonstrated that surface chemistry is determinant in their performance as adsorbent for phenol. Since MCS and MCSFe have very similar oxygen content (see Table 4.7.3), the decrease of the adsorption capacity should be attributed to the difference in the surface area and micropore volume, which is indeed considerable as seen in Table 4.7.2.

In Table 4.7.4, Freundlich parameters from fitting of experimental data are shown. All 1/n values are relatively low, which indicates high affinities between these carbons surfaces and phenol. However, the R^2 value for the fitting of samples MCSFe and GTNFe is lower than that obtained for ME or MCS. The fact that correlations are rather low could be related to the low adsorption capacity of these samples

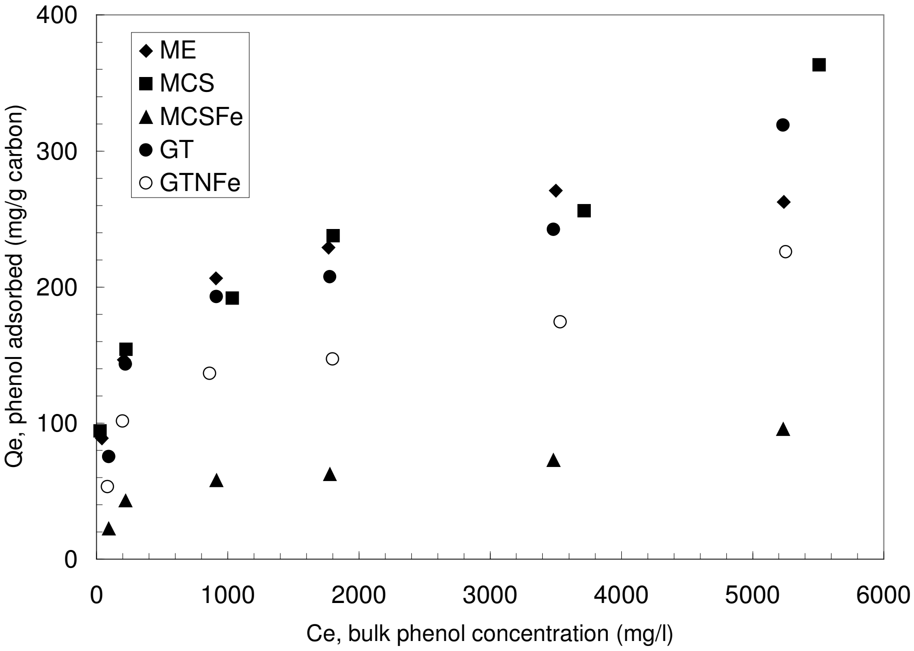


Figure 4.7.2. Phenol adsorption isotherms over tailored activated carbons at 20ºC.

Table 4.7.4. Freundlich parameters for phenol adsorption of the tailored carbons.

Sample	**K** **(mg/g AC)(l/mg)$^{1/n}$**	**1/n**	**R^2**
ME	40	0.23	0.98
MCS	43	0.23	0.96
MCSFe	7	0.30	0.93
GT	22	0.30	0.92
GTNFe	17	0.30	0.93

4.7.3. Catalytic performance of tailored carbons in TBR tests.

The phenol conversions obtained with these tailored carbons in the TBR tests are shown in Figure 4.7.4. The phenol conversion obtained with MCS is practically twice that that obtained with the commercial GT also made from coconut shells, 8% vs. 3.5% respectively, although both are marginal for practical purposes. Regardless of the iron content of sample MCSFe, which is half that of ME (see Table 4.7.3), the conversion achieved with MCSFe is considerably lower, only 10% compared to 45% given by ME. Even when compared to the commercial F400 having similar iron content (see Table 2.2.2), the phenol conversion exhibited by MCSFe is too low, since F400 furnishes 38%. The low catalytic activity could be attributed to the very low value of surface area and low micropore volume developed during activation of this carbon. Actually the value of phenol conversion obtained with MCSFe is practically the same observed for MCS, which suggests that both MCS and MCSFe are affected by serious problems of surface availability.

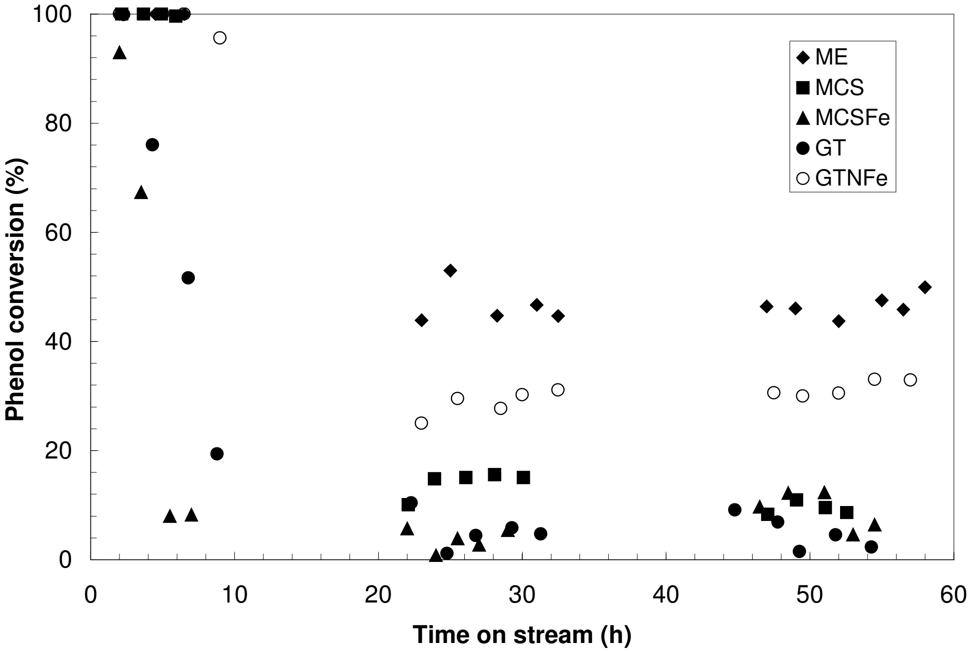


Figure 4.7.3. Phenol conversion in TBR reactor using tailored manufactured samples, at 140ºC and 2 bar of oxygen partial pressure.

On the contrary, sample GTNFe showed a noticeable catalytic activity for phenol oxidation, being clearly superior than the original GT, 33% and 3.5%, respectively. Originally, GT shows no iron content since it is made from coconut shells that is not expected to contain significant amount of iron, unless coming from mineral impurities. Through the acid wash pre-treatment and iron impregnation modification, it was possible to provide this carbon with the same iron content than a commercial carbon made from coal (F400). Despite the surface area of this carbon is half of ME, for instance, its adsorption capacity is very similar (see Figure 4.2.1), which suggests that it has a high volume of micropores. This microporosity and the formation of carboxylic functionalities after acid wash could be responsible for the high amount of iron later fixed in GTNFe with the thermal treatment.

When analysing the amount of acidic compounds formed as intermediates with these carbons, some noticeable observations can be made. With carbon MCS, 33% of the intermediates formed where acids. This value is higher than the 25% observed with carbon GT. This is a low mineralisation that correlates with their poor catalytic performance. However, the amount of acids formed as intermediates of the phenol oxidation pathway considerably increased when iron was incorporated to the carbon, up to 88% and 89% respectively, even in the case of MCSFe, for which the increase of phenol conversion, compared to MCS, is only from 8% to 10%. For GNTFe, the increase of the phenol conversion also produces an improvement in the amount of acidic compounds formed, which reaches 89% in comparison to the 25% from GT.

Leaching of iron also occurred for MCSFe and GTNFe. The iron content in the used activated carbons after 55 hours on stream are listed in Table 4.7.4, as well as the ΔW of all carbons studied in this section, the pH and the iron concentration in the exited effluent at the end of the run. The leaching was about 80% for sample MCSFe and 57%

for GTNFe. Since the iron in the exited effluent is measured at the last sample taken from the reactor and the iron concentration obtained for MCSFe is very low compared to that measured for ME and GTNFe, it is possible to presume that most of the leaching could be occurring during the first hours of operation. Zhu et al. (1997) proposed that during the carbonisation step, iron atoms migrate from the outer surface to the inner part of the bulk of carbon particles. This migration depends on the temperature of the carbonisation. Also time could affect the iron migration in the carbon. However the actual impact of these parameters have not been reported. For MCSFe, the iron impregnation was done before the activation, but after carbonisation. The textural properties of the char could dominate the proposed iron migration, remaining most of it on the external surface, where probably it cannot be properly fixed into the carbonaceous matrix, resulting in faster leaching. The iron supported on GTNFe seems to be more resistant to the acidic operation conditions existing inside the reactor, since the leaching was considerably lower.

The leaching was about 80% for sample MCSFe and 57% for GTNFe. Since the iron in the liquid is measure in the last sample taken from the reactor, and the value measured in the case of MCSFe is very low compared with the one measure in the liquid when using ME and GTNFe, it is possible to think that most of the leaching could be occurring in the first hours of operation. Zhu et al. (1997) proposed that during carbonisation step, iron atoms migrate from the surface to the inner part of the bulk of carbon particles. This migration depends on the temperature of the carbonisation. Also time could be affecting the iron migration in the carbon, however the effect of this parameter has not been reported. In case of sample MCSFe, the iron impregnation was done before the activation, but after carbonisation. The textural properties of the char could be affecting the proposed iron migration, remaining most of it on the surface, where it probably can not be properly fixed in the carbonaceous matrix, with the consequent high percentage of leaching. The iron fixed in GTNFe seems to be more resistant to the acidic conditions of operation inside the reactor, since the leaching was considerably lower.

Table 4.7.5. Weight difference in ME and tailored manufactured samples after operation in TBR and final pH of liquid stream.

Sample	**ΔW (g)**	**Final pH**	**Fe in the outlet effluent (mg/L)**	**Fe content after use (% wt)**
ME	2.519	2.13	9.9	0.31
MCS	2.900	3.85	0.0	0.00
MCSFe	2.051	2.96	0.3	0.04
GT	2.829	3.65	0.0	0.00
GTNFe	3.244	2.49	7.3	0.13

Finally, TOC conversion evolutions in front of time on stream are presented in Figure 4.7.5. Alike for GT, MCSFe gives some negative TOC conversions. This negatives values of conversion, when so low phenol removal is achieved could be attributed to the later release of phenol polymers from the surface, which were attached during the first hours of operation but that are not measured as phenol by means of HPLC, albeit they are later counted when measuring the TOC of the sample.

Since negatives values of TOC conversion were obtained with samples GT and MCSFe, is difficult to calculate the difference with phenol conversion. In any case, samples MCS and GTNFe showed difference with phenol conversion, 2% and 18% respectively. This later value is even higher than the 13% of difference observed for ME. This indicates that the incorporation of iron in carbon GT increases not only the phenol conversion and the formation of acids as intermediates. It also improves the selectivity towards CO_2.

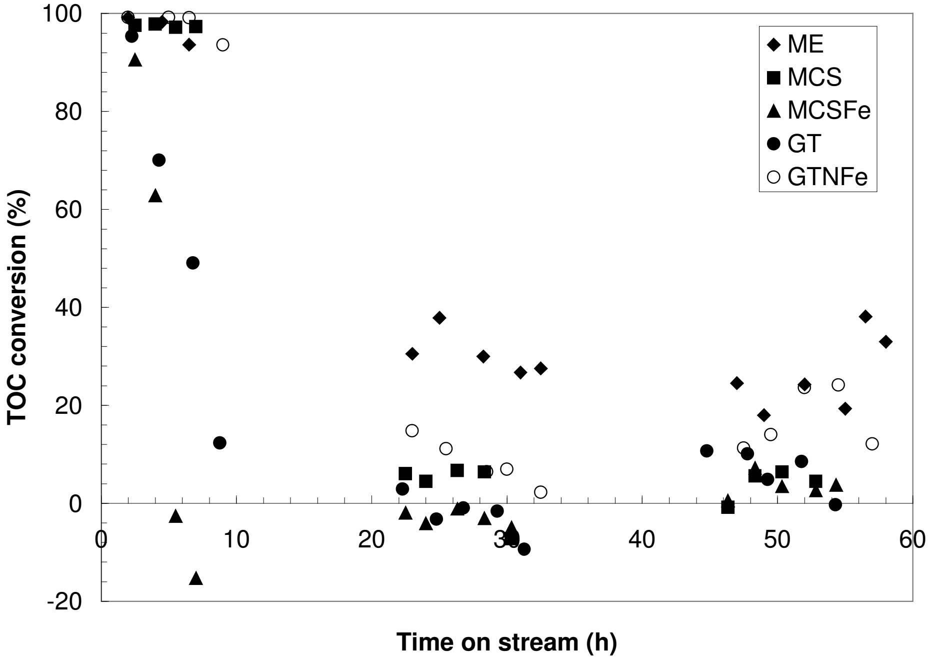


Figure 4.7.4. TOC conversion in TBR reactor using tailored manufactured samples, at 140ºC and 2 bar of oxygen partial pressure.

In summary, coconut shells can be successfully used to produce activated carbons with mechanical stability to resist the operation conditions inside the TBR. Also, the one-step pyrolysis with steam produces highly microporous materials. However, in order to furnish catalytic activity for phenol oxidation, it is necessary to incorporate iron. The results demonstrate that in order to have iron catalytically active is desirable to incorporate it by impregnation after activation, since the oxidative environment during the activation step could give a non catalytically active iron phase.

Chapter V

Conclusions and future work

5.1. General conclusions

The main conclusions derived from this investigation are summarised as follows.

1. Thermal treatments under inert atmosphere are effective in eliminating oxygen surface functionalities present in the activated carbon, which are formed during activation. Thus, after treatment at 900ºC, the predominant remaining groups are carbonyls and other oxygenated functionalities with basic character. The treatment under hydrogen was effective not only for removing these oxygen groups, but also for stabilising the carbon surface, as hydrogen reacts with the reactive sites remaining after the decomposition of the surface oxygen groups.
2. The removal of the more acidic surface oxygen groups improves the phenol adsorption capacity because it enhances the mechanisms proposed as responsible for the phenol adsorption on AC. On the one hand, it favours the formation of donor-acceptor complexes between the phenol aromatic ring acting as acceptor and the remaining carbonyls in the AC surface acting as electron donors. On the other hand, there is an increase of the π-π interactions between the π electrons of the carbon basal plane and the phenol aromatic ring.
3. Also, the reduction of the surface acidity by outgassing the surface oxygen groups reduces the hydrophilic character of the carbon surface, avoiding the formation of water clusters (i.e. the solvent effect) that block the active sites for the phenol adsorption. This acidity reduction was evidenced by the high pH_{pzc} values shown by all the activated carbons thermally treated either under nitrogen or hydrogen.
4. Thermal treatments did not modify the textural properties, i.e. surface area and pore volume of the activated carbons. This means that the phenol adsorption capacity of a carbonaceous material can be improve by a physical treatment that actually did not alter its porosity.
5. However, both the improvement of the adsorption capacity and the removal of surface oxygen groups did not substantially alter the catalytic performance in comparison with that shown by the parent activated carbon. This suggests that the chemical properties of the activated carbon surface and the improved adsorption capacity are not the key factor for its catalytic activity.
6. Neither mesopore volume did seem to decisively contribute to the catalytic activity shown by activated carbons. Samples derived from HD carbon, which are highly mesoporous, showed a poor catalytic activity. Only a slight increase in the conversion obtained with HDDSH was observed and it is rather attributed to the formation of phenolic polymeric compounds attached to the surface, which could be promoted by the enhanced meso and microporosity of this sample allowing a higher phenol adsorption during the first hours of operation in the reactor.

However, sample MESCa, which also have a higher mesopore volume than its parent ME, did not show any improvement in its capacity to oxidise phenol, since the conversion obtained with these two carbons is practically identical, 42% and 45%, respectively.

7. The demineralisation of sample ME produces an important decrease in the phenol conversion, from 45% down to 25%. This result demonstrates that mineral matter, more specifically iron that is the metal found in higher amount in this carbon, has a great influence in the catalytic activity of this material. This is confirmed by the fact that, three commercial ACs with high surface area and high micropore volume, but with no mineral matter present due to its raw material, show no catalytic behaviour in the oxidation of phenol.
8. Iron content of the activated carbon has proven to correlate with the catalytic performance for CWAO of phenol in a TBR. By increasing 3.5 times the amount of iron in the parent carbon ME, it is possible to increase the phenol conversion up to 80% as for MENFe and MESCaFe.
9. The location of the iron in the activated carbon matrix seems to be critical for the subsequent catalytic behaviour in phenol oxidation. Assays done with several commercial activated carbons demonstrate that despite having the same iron content, two carbons like ME and CN exhibit different catalytic behaviour, giving different conversions (45% and 30% respectively), although both remarkable. Different selectivity for the formation of partial oxidation compounds was found, too. This appears to indicate that not only the content of iron is necessary in order to show catalytic behaviour, but it is also needed that iron to be available in a suitable form to actually perform as catalyst.
10. One-step pyrolysis procedure was effective to manufacture activated carbon from coconut shells, achieving high values of surface area and well developed porosity, although most of the porous being in the range of microporosity. MCS carbon, despite having 34% lower surface area, shows the same adsorption capacity than commercial carbons like ME made from coal or GT which is also made of coconut shells. However, due to the absence of mineral matter in the sample made from coconut shells, carbon MCS did not show any catalytic performance. Sample MCSFe, made also from coconut shells with an iron impregnation step included before the activation, shows also lack of catalytic behaviour as MCS. This indicates that, despite having similar iron content than IR or F400, two commercial AC made from coal, the iron in sample MCSFe is not catalytically active. In conclusion, the iron in the carbonaceous materials does not always show catalytic activity, probably due to the position or even the crystalline phase in which it is present.
11. Iron impregnation is more effective when the carbonaceous materials have been previously treated with acid to form addition surface acidic groups. These acidic groups exhibit ion exchange properties enhancing the iron adsorption onto the surface, later fixed by the gasification under nitrogen.
12. It was possible to incorporate iron to a commercial activated carbon made from coconut shells, GT, that showed nil catalytic activity in the CWAO of phenol. The iron content, initially negligible, was increased up to 0.3% wt. This iron impregnated carbon, GTNFe, was capable of oxidising phenol and gave a conversion of 30% at steady state.

5.2. Future work

The most relevant finding of this research work is that the iron content of activated carbon is the main responsible for the catalytic activity shown by this material, despite other parameters probably affects the catalytic performance.

However, the location of iron in the carbonaceous structure and perhaps its crystalline phase seem to be determinant in the behaviour of this metal as catalyst. In this study, none of these two parameters were deeply studied. So, in order to design experimental procedures to manufacture activated carbons with appropriate catalytic properties it, is necessary to fully identify the suitable location of iron and its optimum state and optimising the protocols of preparation. Moreover, highly mesoporous activated carbons should be designed for this purpose.

It would be also necessary to evaluate the performance of the iron impregnated carbons and their stability-durability at different conditions in TBR. A complete screening of the temperature, oxygen partial pressure and space time effect is needed in order to assess the yielded product distribution, which should be suitable for posterior biotreatment. In addition, kinetics are needed for a subsequent design of scaled reactors.

As metal content is believed to be critical for wet oxidation applications of the activated carbons, other raw materials for their preparation like petroleum coke could be of interest because of its natural high metal content.

An interesting research opportunity is the development of hybrid materials, like zeolite/carbon composites that include iron in the zeolite. This material could show several advantages when compared to Fe supported over activated carbon. For instance, it would have both hydrophilic and hydrophobic character, since the presence of the zeolite will increase the hydrophilicity of the material. Also, due to the more organised structure of the zeolite, it could be easier to locate the iron in the structure in positions that favour the catalytic activity, whereas the activated carbon would serve for enhancing the generation of oxygen radicals form the molecular oxygen.

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Annex A

In this Annex are collected the pH profiles of the liquid samples from TBR experiments of all the carbons used in this work.

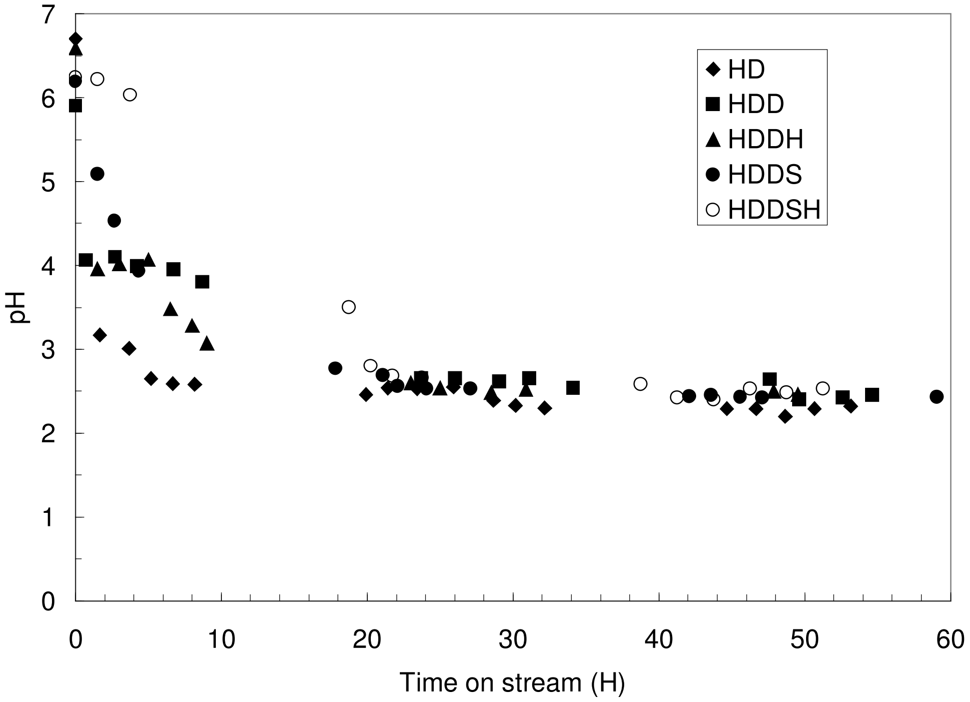

Figure A.1. pH profile of liquid samples from TBR for HD's carbons.

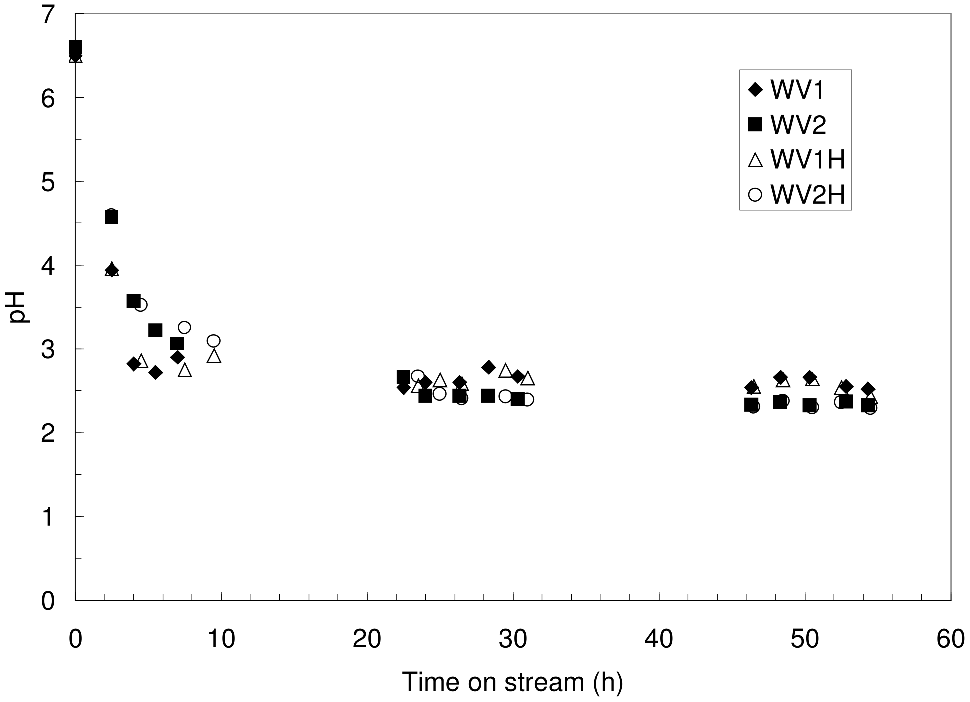

Figure A.2. pH profile of liquid samples from TBR for WV's carbons.

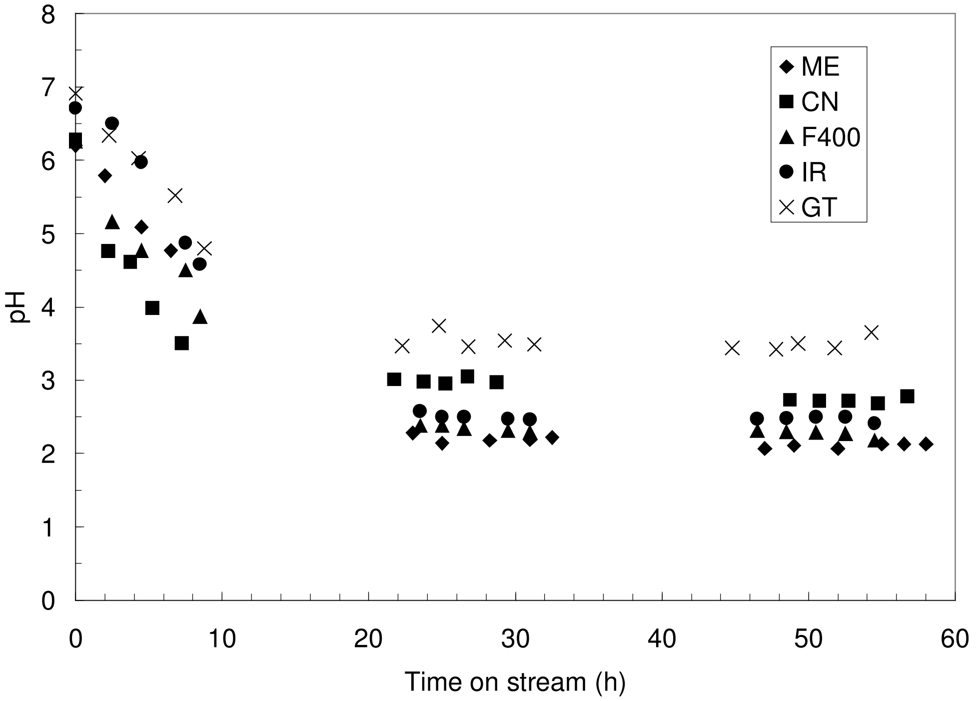

Figure A.3. pH profile of liquid samples from TBR for commercial ACs.

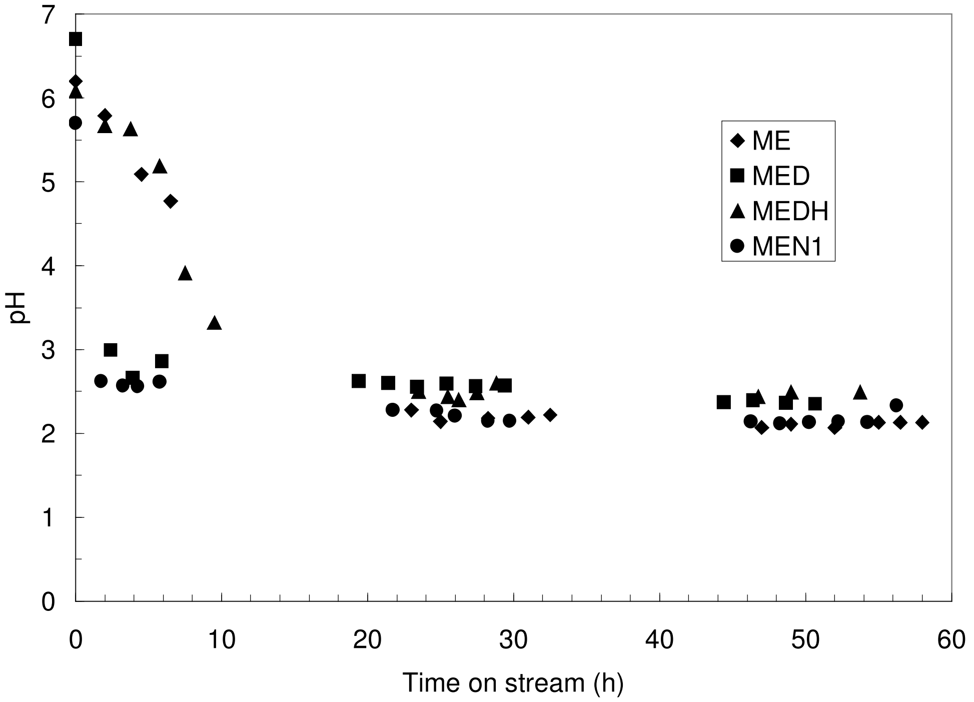

Figure A.4. pH profile of liquid samples from TBR for acid washed ACs.

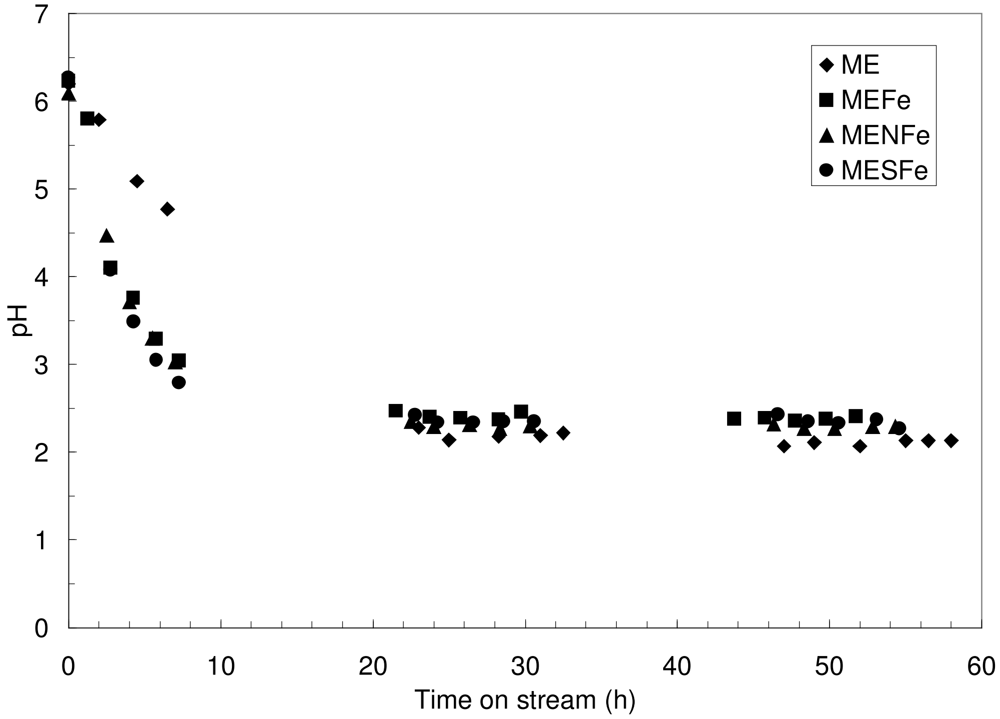

Figure A.5. pH profile of liquid samples from TBR for iron impregnated ACs.

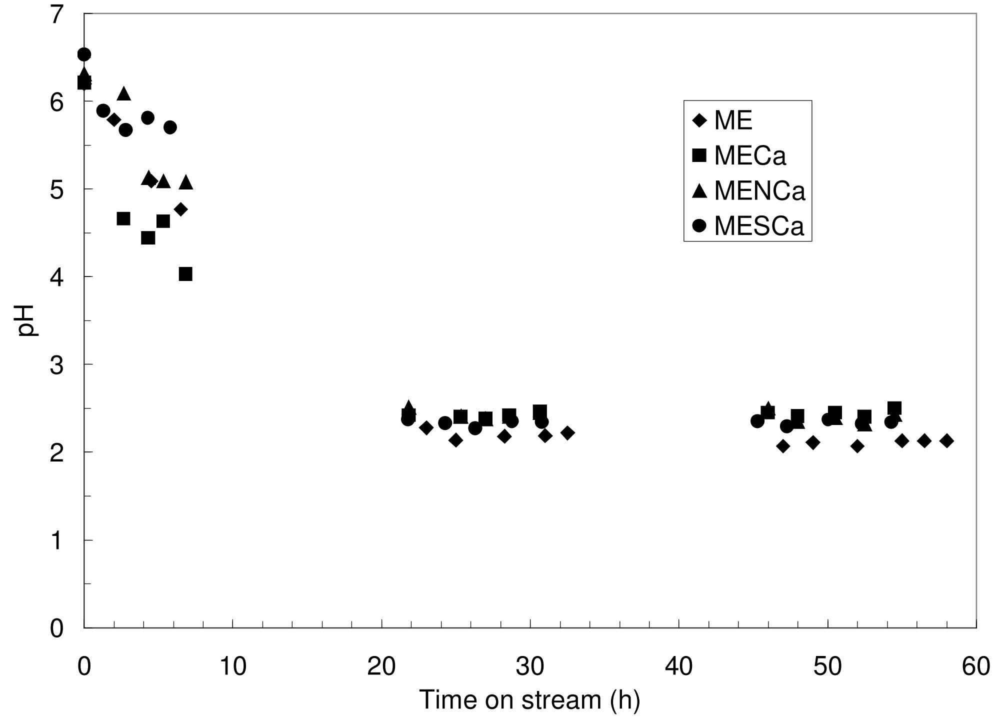

Figure A.6. pH profile of liquid samples from TBR for calcium impregnated ACs.

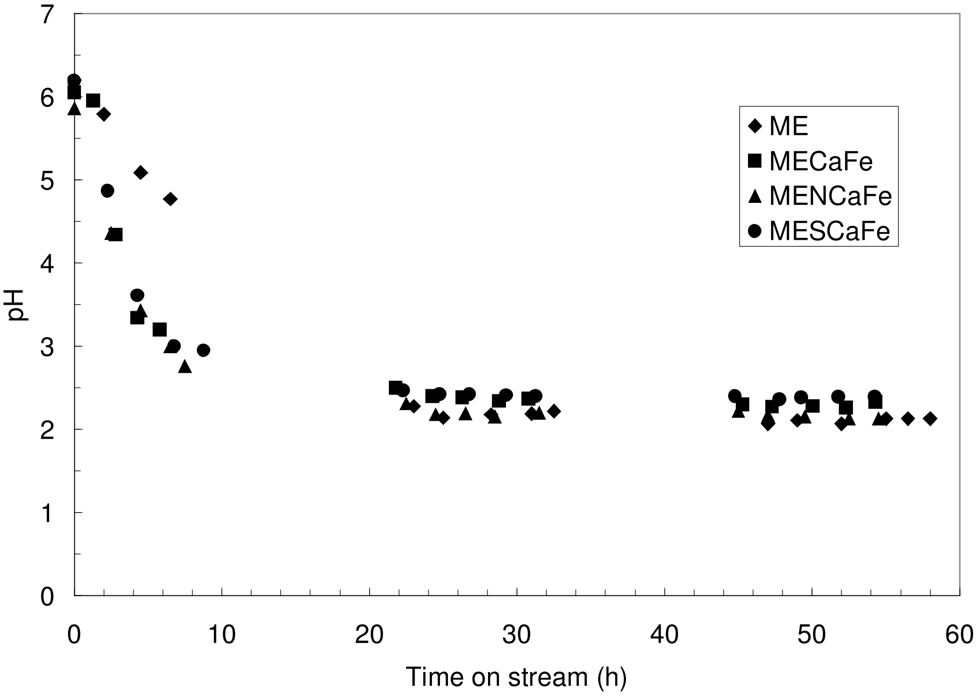

Figure A.7. pH profile of liquid samples from TBR for iron and calcium impregnated ACs.

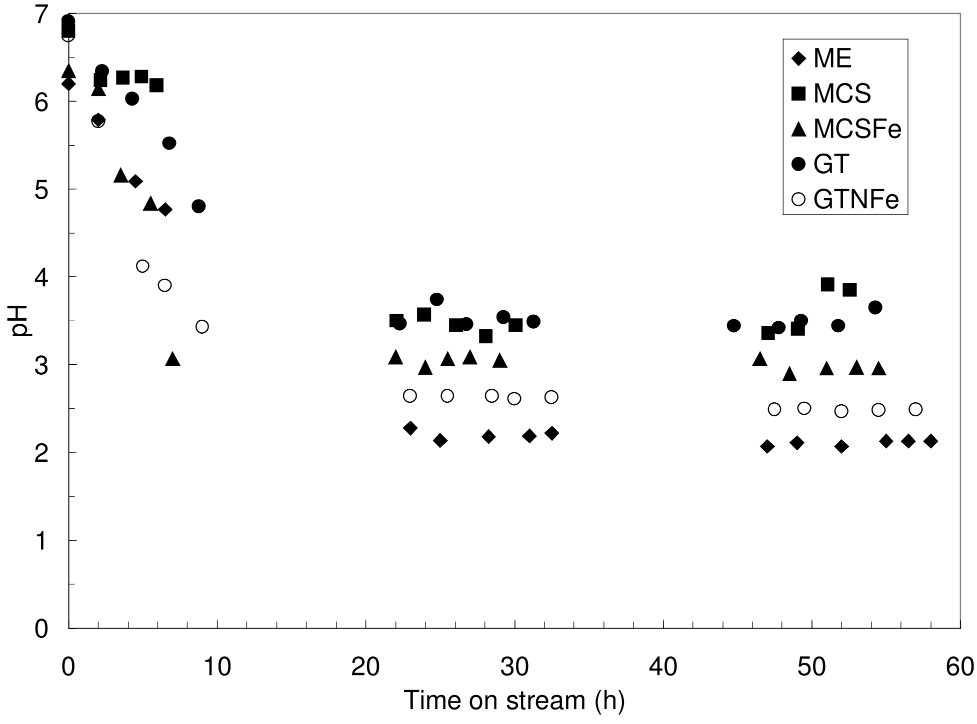

Figure A.8. pH profile of liquid samples from TBR for tailored ACs.