UNIVERSITAT ROVIRA I VIRGILI

HOMOGENEOUS AND HETEROGENEOUS AQUEOUS PHASE OXIDATION OF PHENOL WITH FENTON-LIKE PROCESSE.

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DOCTORAL THESIS

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Departament d'Enginyeria Química

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Tarragona, July 2014

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UNIVERSITAT ROVIRA I VIRGILI

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UNIVERSITAT ROVIRA I VIRGILI

Supervised by Dr. Josep Font Capafons

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor from the Universitat Rovira i Virgili in the Chemical, Environmental and Process Engineering programme.

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I, Dr. Josep Font Capafons, associate professor in the Department of Chemical Engineering of the Rovira i Virgili University,of the Rovira i Virgili University,

CERTIFY:

That the present study, entitled ”**Homogeneous and heterogeneous aqueous phase oxidation of phenol with Fenton's-like processes**”, presented by Mrs SELAMAWIT ASHAGRE MESSELE for the award of the degree of Doctor, has been carried out under my supervision at the Department of Chemical Engineering of this university, and that it fulfils all the requirements to be eligible for the International Doctorate Label.

Dr. Josep Font Capafons

Tarragona, 12th June 2014

To my beloved family, especially to **ESKIE**, **BLEINE** and **…**

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Summary

Wastewater can basically be divided in two major categories: urban and industrial. In the case of urban effluents, the main pollutant load is mostly non toxic and biodegradable. This kind of wastewater is mainly treated through biological treatment, which is sufficient and the most economic solution for this problem. On the contrary, industrial effluents encounter refractory and/or biotoxic compounds, which need a specific chemical treatment in order to eliminate or at least partly reduce the toxic concentration to the required level allowing for direct discharge to conventional sewage sludge plants. Examples of toxic and non-biodegradable pollutants are phenols, surfactants, chlorinated compounds, pesticides, and aromatic hydrocarbons, among many others.

In the last decades, various chemical oxidation techniques have been developed to overcome the inconveniences of conventional treatment methods, in particular for dealing with industrial wastewaters. Among these techniques, advanced oxidation processes (AOPs) appear to be a promising field of study, which have been reported to be effective for the degradation of soluble organic contaminants from waters, surface waters, soils and wastewaters containing non-biodegradable organic pollutants, because they can often provide an almost total degradation, under reasonably mild conditions of temperature and pressure. One of the most promising AOPs is the Fenton process. Fenton's reagent uses Fe ions as homogeneous catalysts, and the reagent hydrogen peroxide producing hydroxyl and perhydroxyl radicals. The hydroxyl radicals (HO•) produced will then attack the organic matter present in the reaction medium, the hydroxyl radical being a powerful inorganic oxidant that non-selectively reacts with numerous compounds.

This work is specially focused in homogeneous and heterogeneous oxidation of phenol with Fenton-like process, which is supposed to mainly give rise to hydroxyl radicals after catalytic decomposition.

The main factor that influences the Fenton processes is the solution pH. The optimum pH for the Fenton reaction has been repeatedly reported to be around 3. The main reason for lower efficiency of Fenton reaction at higher pH value (pH > 4) is due to the precipitation of ferric oxyhydroxide or ferric hydroxide, which is not active in catalytic activity. In this situation, less free iron ions are available to catalytically decompose hydrogen peroxide and less hydroxyl radicals are accordingly generated. Therefore, in order to achieve the optimum process efficiency, the solution pH should be controlled by the addition of huge amounts of acid. This makes the process

unsuitable for many applications. As an alternative for the above drawbacks, this thesis (Chapter 3) illustrates how the addition of organic ligands (EDTA and others) can complex the iron and enables the process to be carried out at neutral pH in homogeneous Fenton system. The results demonstrate that the proposed alternative approach allows extending the capacity of degrading phenol from the usual acidic pH (around 3.0) to circumneutral pH range (6.5-7.5). The overall feasibility of the process depends on the chelating agent concentration and the initial pH of the solution. Improvement on the phenol removal efficiency at neutral pH also occurs for the other chelating agents tested.

Fenton processes can also be carried out under heterogeneous conditions (catalytic wet peroxide oxidation, CWPO) by immobilizing the iron catalyst on a support, such as activated carbon (AC) and carbon xerogel. The main drawbacks of homogeneous Fenton process are firstly, its pH sensitivity and secondly, the need for a final separation of soluble iron species from the treated water. Neutralization or even flocculation units are usually necessary to remove the active iron species in form of iron sludge. These drawbacks have promoted the development of Fenton processes based on heterogeneous catalytic systems, prepared by impregnating iron or iron oxides into porous supports. The most important issue in the heterogeneous Fenton process is the development of a heterogeneous catalyst with high activity and long-term stability at a reasonable cost. Among the porous solids, carbon materials have been used for long time in heterogeneous catalysis, either as direct catalysts or as a support.

Therefore, the main part of the doctoral thesis (Chapter 4 to Chapter 7) is focused on heterogeneous Fenton systems using zero-valent iron (ZVI) supported on different carbon materials such as activated carbon and carbon xerogels. Chapter 4 illustrates that the catalytic activity towards phenol degradation was found to be enhanced by nano scale zero-valent iron supported on activated carbon catalysts (nZVI/AC) compared to that of Fe/AC, because, in the case of nZVI/AC catalysts, the iron is in the zero valent state, which has an advantage for Fenton chemistry. The main advantage of this alternative is a faster recycling of ferric iron into ferrous species at the metallic iron surface, so that they are more readily available throughout the reaction time.

Moreover, ZVI supported catalysts were prepared through modifying an activated carbon support with different nitrogen containing precursors (ethylenediamine, urea and melamine) and impregnating it with 3 wt% of iron. The results from the different characterization techniques demonstrate that the nitrogen-containing groups are successfully introduced into the carbon surface via all the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. Both surface chemistry and textural properties of carbons are influenced by the nitrogen source and the type of oxygen functionalities preexisting on the surface. The modified carbons supported iron catalysts revealed significantly enhanced phenol removal efficiency, showing interesting catalytic stability.

On the other hand, activated carbons with different amounts of surface oxygenated groups were used as adsorbents or supports for zero-valent iron catalyst and tested in phenol adsorption and catalytic wet peroxide oxidation, respectively. The results revealed that the surface chemistry of the support plays an important role in phenol adsorption and in the catalytic performance of the respective iron-supported catalysts. ZVI is active when the support has only a limited amount of oxygenated groups on the surface. The presence of acidic oxygenated surface groups is not favorable for the catalytic activity of ZVI in phenol oxidation as well as for phenol adsorption. ZVI supported on activated carbon heat-treated at 900 ºC yields the best phenol removal.

Finally, nitrogen-free carbon xerogels prepared at different pH and nitrogen-containing carbon xerogel materials from urea and melamine precursors were prepared and evaluated as adsorbents/catalysts in the removal of phenol. Then, ZVI was supported on these prepared carbon xerogel materials and its activity was evaluated for phenol removal by adsorption and CWPO. The prepared samples were characterized by determining the N_2 adsorption isotherms at -196 ºC, the pH at the point of zero charge and the elemental analysis. The textural properties of the pure and nitrogen-containing carbon xerogels are strongly influenced by the pH of the preparation solution and precursor used. The presence of ZVI in all carbon xerogel supports improved the phenol removal efficiency. However, ZVI supported on urea and melamine treated carbon xerogel at pH of 5.3 (ZVI/CXU-5.3 and ZVI/CXM-5.3) showed a good performance, reaching above 87% phenol conversion after 60 min of CWPO. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e. CXU-5.3 and CXM-5.3) shows low removal efficiency, below 5% after 60 min. The presence of ZVI on N-containing catalysts yields a better phenol removal, reaching values over 93% after 3 h, especially for those carbon xerogels having high nitrogen content (ZVI/CXM-5.3 and ZVI/CXM-6.9).

Sumario

Las aguas residuales básicamente se pueden dividir en dos grandes categorías: urbana e industrial. En el caso de los efluentes urbanos, la principal carga contaminante es principalmente biodegradable y no tóxica. Esta clase de agua residual es habitualmente tratada a través de procesos biológicos, lo cual es suficiente y la solución más económica para este problema. Por el contrario, los efluentes industriales portan compuestos bioxenóticos y/o recalcitrantes, que necesitan un tratamiento químico específico a fin de eliminar o al menos reducir parcialmente la concentración de tóxicos al nivel requerido para permitir una descarga directa a plantas convencionales de lodos activados. Ejemplos de contaminantes tóxicos y no biodegradables son fenoles, surfactantes, compuestos clorados, pesticidas e hidrocarburos aromáticos, entre otros muchos.

En las últimas décadas, se han desarrollado diversas técnicas, basadas en la oxidación, a fin de superar los inconvenientes de los métodos de tratamiento convencionales, en particular para las aguas residuales industriales. Entre estas técnicas, los procesos de oxidación avanzada (AOPs) aparecen como un prometedor campo de estudio, ya que han demostrado ser eficientes para la degradación de contaminantes orgánicos solubles en aguas, aguas superficiales, suelos y aguas residuales que contienen substancias orgánicas no biodegradables, puesto que frecuentemente pueden proporcionar una casi total degradación, bajo condiciones de presión y temperatura razonablemente suaves. Una de las más prometedoras AOPs es el proceso Fenton. El licor de Fenton aplica cationes de Fe como catalizador homogéneo y peróxido de hidrógeno como oxidante, que genera radicales hidroxilo y perhidroxilo. El radical hidroxilo (HO•) producido ataca la materia orgánica presente en el medio de reacción, puesto que es un potente oxidante inorgánico que reacciona no selectivamente con numerosos compuestos.

Este trabajo se focaliza especialmente en la oxidación homogénea y heterogénea de fenol mediante procesos basados en la química Fenton, es decir, que principalmente generan radicales hidroxilo por descomposición catalítica.

El principal factor que influencia los procesos Fenton es el pH de la solución. El pH óptimo se ha establecido repetidamente alrededor 3. La principal razón para la baja eficacia de la reacción Fenton es un pH alto (pH > 4) y es debido a la precipitación de hidróxido u oxihidróxido férrico, no activo como catalizador. En esta situación, menos cationes libres de

hierro están disponibles para descomponer catalíticamente el peróxido de hidrógeno y, consecuentemente, se generan menos radicales hidroxilo. En consecuencia, para una eficiencia óptima del proceso, el pH de la solución debe ser controlado por la adición de enormes cantidades de ácido. Este consumo hace el proceso inadecuado para muchas aplicaciones. Como una alternativa para los citados inconvenientes, esta tesis (capítulo 3) ilustra como la adición de agentes quelantes orgánicos (EDTA y otros) puede complejar el hierro y permite que el proceso pueda llevarse a cabo a pH cercanos a la neutralidad en un sistema homogéneo. Los resultados demuestran que la alternativa propuesta permite extender la capacidad de degradar fenol desde el pH ácido clásico (alrededor de 3) hasta más allá del pH neutro (6.5-7.5). La viabilidad global del proceso depende de la concentración de agente quelante y el pH inicial de la solución. La mejora de la capacidad de eliminación a pH neutro también se ha constatado para los otros agentes quelantes ensayados.

Los procesos Fenton también pueden llevarse a cabo bajo condiciones heterogéneas (CWPO) por inmovilización del catalizador de hierro sobre un soporte, como por ejemplo el carbón activado o un xerogel de carbono. Los principales inconvenientes del proceso Fenton homogéneo son, en primer lugar, la sensibilidad al pH y, después, la necesidad de una separación final de las especies de hierro solubles en el agua tratada. Así, se precisan de unidades de neutralización y floculación para recuperar las especies activas de hierro en forma de fango de hierro. Estos inconvenientes han promovido el desarrollo de procesos Fenton basados en sistemas catalíticos heterogéneos, preparados por impregnación de hierro u óxidos de hierro sobre soportes porosos. El tema más importante en el proceso Fenton heterogéneo es el desarrollo de un catalizador heterogéneo con una alta actividad y una estabilidad de larga duración a un coste razonable. Entre los sólidos porosos, los materiales carbonosos se han utilizado desde hace tiempo en catálisis heterogénea, ya sea como catalizador directo o soporte.

En consecuencia, la mayor parte de la tesis (capítulos 4 a 7) se centra en sistemas Fenton heterogéneos utilizando hierro cerovalente (ZVI) soportado sobre diferentes materiales carbonosos tales como el carbón activado (AC) o el xerogel de carbono. El capítulo 4 presenta como la actividad catalítica hacia la degradación de fenol se incrementó mediante catalizadores de nanohierro cerovalente sobre carbón activado (nZVI/AC) en comparación con los Fe/AC clásicos, ya que, en el caso de los catalizadores nZVI/AC, el hierro en su estado de valencia cero presenta una clara ventaja para la química Fenton, esto es, una más rápida reducción del hierro férrico a hierro ferroso a través de la superficie de hierro metálico, de forma que su concentración se mantiene más elevada durante el tiempo de reacción.

Además, los catalizadores soportados de ZVI se prepararon por modificación del soporte de carbón activado mediante diferentes precursores nitrogenados (etilendiamina, urea y melamina) e impregnación con hierro al 3%. Los resultados de las diferentes técnicas de caracterización demuestran que los grupos nitrogenados se consiguieron introducir sobre la superficie del carbón activado a partir de los precursores. Los tests de los diferentes carbones modificados como adsorbentes o catalizadores indicaron que la capacidad de adsorción y la eficiencia en la oxidación de fenol se gobernaban por el área superficial específica y los grupos funcionales presentes. Tanto la química superficial como las propiedades texturales dependen de la fuente del nitrógeno y las funcionalidades oxigenadas originalmente presentes en la superficie. Los catalizadores de hierro soportados sobre carbones modificados proporcionaron una significativa mejora de la eficiencia en la eliminación de fenol, demostrando una interesante estabilidad catalítica.

Por otro lado, carbones activados con diferentes contenidos de grupos superficiales oxigenados se ensayaron como adsorbentes o soportes de ZVI para la adsorción de fenol o su oxidación con peróxido de hidrógeno. Los resultados muestran que la química superficial de los soportes representa un importante papel tanto en la adsorción de fenol como en sus prestaciones catalíticas cuando contienen hierro soportado. El ZVI es activo cuando el soporte posee un contenido limitado de grupos oxigenados en la superficie. La presencia de grupos oxigenados ácidos superficiales no favorece la actividad catalítica del ZVI para la oxidación del fenol, ni para su adsorción. El ZVI soportado sobre carbones activados tratados térmicamente hasta 900 ºC rinde la mejor eliminación de fenol.

Finalmente, se prepararon xerogeles de carbono sin nitrógeno a diferentes pHs y también xerogeles de carbono con nitrógeno a partir de urea o melamina como precursores, los cuales fueron evaluados como adsorbentes y como catalizadores para la eliminación de fenol. Posteriormente, se soportó sobre ellos ZVI y su actividad fue también evaluada para adsorción y CWPO. Las muestras se caracterizaron determinando las isotermas de adsorción de N_2 a -196 ºC, el pH en el punto de carga cero y análisis elemental. Las propiedades texturales tanto de los xerogeles puros como de los que contienen nitrógeno dependen fuertemente del pH de la solución de preparación y el precursor utilizado. La presencia de ZVI en todos los xerogeles de carbono mejoró su capacidad para eliminar fenol. Sin embargo, el ZVI soportado sobre xerogeles de carbono tratados con urea y melamina a pH 5.3 (ZVI/CXU-5.3 y ZVI/CXM-5.3) mostraron unas prestaciones buenas, alcanzando más del 87% de conversión de fenol después de 60 min de CWPO. Por el contrario, la eliminación de fenol por simple adsorción o CWPO utilizando los mismos materiales en ausencia de ZVI (CXU-5.3 y CXM-5.3) proporcionaron una baja eficiencia de eliminación, por debajo del 5% después de 60 min. En conclusión, la presencia de ZVI sobre catalizadores que contienen nitrógeno rinde una mejor eliminación de fenol, que llega a valores por encima del 93% después de 3 h, especialmente para aquellos xerogeles de carbono con mayor contenido de nitrógeno (ZVI/CXM-5.3 y ZVI/CXM-6.9).

Sumari

Les aigües residuals bàsicament es poden dividir en dos grans categories: urbana i industrial. En el cas dels efluents urbans, la principal càrrega contaminant és principalment biodegradable i no tòxica. Aquesta classe d'aigua residual és habitualment tractada a través de processos biològics, cosa que és suficient i la solució més econòmica per a aquest problema. Pel contrari, els efluents industrials porten compostos bioxenòtics y/o recalcitrants, que necessiten un tractament químic específic a fi d'eliminar o almenys reduir parcialment la concentració de tòxics al nivell requerit per a permetre una descàrrega directa a plantes convencionals de fangs activats. Exemples de contaminants tòxics i no biodegradables són fenols, surfactants, compostos clorats, pesticides i hidrocarburs aromàtics, entre altres molts.

A les últimes dècades, s'han desenvolupat diverses tècniques, basades en l'oxidació, a fi de superar els inconvenients dels mètodes de tractament convencionals, en particular per a les aigües residuals industrials. Entre aquestes tècniques, els processos d'oxidació avançada (AOPs) apareixen com un prometedor camp d'estudi, ja que han demostrat ser eficients per a la degradació de contaminants orgànics solubles en aigües, aigües superficials, sòls i aigües residuals que contenen substàncies orgàniques no biodegradables, atès que freqüentment poden proporcionar una quasi total degradació, sota condicions de pressió i temperatura raonablement suaus. Una de les més prometedores AOPs és el procés Fenton. El licor de Fenton aplica cations de Fe com a catalitzador homogeni i peròxid d'hidrògen com a oxidant, que genera radicals hidroxil i perhidroxil. El radical hidroxil (HO•) produït ataca la matèria orgànica present en el medi de reacció, donat que és un potent oxidant inorgànic que reacciona no selectivament amb nombrosos compostos.

Aquest treball es focalitza especialment en l'oxidació homogènia i heterogènia de fenol mitjançant processos basats en la química Fenton, és a dir, que principalment generen radicals hidroxil per descomposició catalítica.

El principal factor que influencia els processos Fenton és el pH de la solució. El pH òptim s'ha establert repetidament al voltant de 3. La principal raó per a la baixa eficàcia de la reacció Fenton és un pH alt (pH > 4) i es deu a la precipitació d'hidròxid o oxihidròxid fèrric, no actiu com a catalitzador. En aquesta situació, menys cations lliures de ferro estan disponibles per descompondre catalíticament el peròxid d'hidrogen i, conseqüentment, es generen menys radicals hidroxil. Per tant, per a una eficiència òptima del procés, el pH de la solució ha de ser controlat amb

l'addició d'enormes quantitats d'àcid. Aquest consum fa el procés inadequat per a moltes aplicacions. Com una alternativa per als citats inconvenients, aquesta tesi (capítol 3) il·lustra com l'addició d'agents quelants orgànics (EDTA i altres) pot complexar el ferro i permet que el procés pugui portar-se a terme a pH propers a la neutralitat en un sistema homogeni. Els resultats demostren que l'alternativa proposada permet estendre la capacitat de degradar fenol des de el pH àcid clàssic (al voltant de 3) fins a més allà del pH neutre (6.5-7.5). La viabilitat global del procés depèn de la concentració d'agent quelant i el pH inicial de la solució. La millora de la capacitat d'eliminació a pH neutre també s'ha constatat per als altres agents quelants assatjats.

Els processos Fenton també poden dur-se a terme sota condicions heterogènies (CWPO) per immobilització del catalitzador de ferro sobre un soport, com per exemple el carbó activat o un xerogel de carboni. Els principals inconvenients del procés Fenton homogeni són, en primer lloc, la sensibilitat al pH i, després, la necessitat d'una separació final de les espècies de ferro solubles en l'aigua tractada. Així, es precisen d'unitats de neutralització i floculació per recuperar les espècies actives de ferro en forma de fang de ferro. Aquests inconvenients han promogut el desenvolupament de processos Fenton basats en sistemes catalítics heterogenis, preparats per impregnació de ferro o òxids de ferro sobre suports porosos. El tema més important en el procés Fenton heterogeni és el desenvolupament d'un catalitzador heterogeni amb una alta activitat i una estabilitat de llarga durada a un cost raonable. Entre els sòlids porosos, els materials carbonosos s'han utilitzat des de fa temps en catàlisi heterogènia, ja sigui com a catalitzador directe o suport.

En conseqüència, la major part de la tesi (capítols 4 a 7) se centra en sistemes Fenton heterogenis utilitzant ferro zerovalent (ZVI) suportat sobre diferents materials carbonosos tals com el carbó activat (AC) o el xerogel de carboni. El capítol 4 presenta com l'activitat catalítica per a la degradació de fenol es va incrementar mitjançant catalitzadors de nanoferro zerovalent sobre carbó activat (nZVI/AC) en comparació amb els Fe/AC clàssics, ja que, en el cas dels catalitzadors nZVI/AC, el ferro en el seu estat de valència zero presenta una clara avantatge per a la química Fenton, això és, una més ràpida reducció del ferro fèrric a ferro ferròs a través de la superfície de ferro metàl·lic, de forma que la seva concentració es manté més elevada durant el temps de reacció.

A més, els catalitzadors suportats de ZVI es van preparar per modificació del suport de carbó activat mitjançant diferents precursors nitrogenats (etilendiamina, urea i melamina) i impregnació amb ferro al 3%. Els resultats de les diferents tècniques de caracterització demostren que els grups nitrogenats es van aconseguir introduir sobre la superfície del carbó activat a partir dels precursors. Els tests dels diferents carbons modificats com a adsorbents o catalitzadors van indicar que la capacitat d'adsorció i la eficiència en l'oxidació de fenol eren governats per l'àrea superficial específica i els grups funcionals presents. Tant la química superficial com les propietats texturals depenen de la font del nitrogen i les funcionalitats oxigenades originalment presents en la superfície. Els catalitzadors de ferro suportats sobre carbons modificats van proporcionar una significativa millora de l'eficiència en l'eliminació de fenol, demostrant una interessant estabilitat catalítica.

D'una altra banda, carbons activats amb diferents continguts de grups superficials oxigenats es van assajar com a adsorbents o suports de ZVI per a l'adsorció de fenol o la seva oxidació amb peròxid d'hidrogen. Els resultats mostren que la química superficial dels suports representa un important paper tant en l'adsorció de fenol com a les seves prestacions catalítiques quan contenen ferro suportat. El ZVI és actiu quan el suport posseeix un contingut limitat de grups oxigenats a la superfície. La presència de grups oxigenats àcids superficials no afavoreix l'activitat catalítica del ZVI per a l'oxidació del fenol, ni per a la seva adsorció. El ZVI suportat sobre carbons activats tractats tèrmicament fins a 900 ºC rendeix la millor eliminació de fenol.

Finalment, es van preparar xerogels de carboni sense nitrogen a diferents pHs i també xerogels de carboni amb nitrogen a partir d'urea o melamina com a precursors, els quals van ser avaluats com a adsorbents i com a catalitzadors per a l'eliminació de fenol. Posteriorment, es va suportar sobre ells ZVI i la seva activitat va ser també avaluada per a adsorció i CWPO. Les mostres es van caracteritzar determinant les isotermes d'adsorció de N_2 a -196 ºC, el pH en el punt de càrrega zero i anàlisi elemental. Les propietats texturals tant dels xerogels purs com dels que contenen nitrogen depenen fortament del pH de la solució de preparació i el precursor utilitzat. La presència de ZVI en tots els xerogels de carboni va millorar la seva capacitat per eliminar fenol. De totes formes, el ZVI suportat sobre xerogels de carboni tractats amb urea i melamina a pH 5.3 (ZVI/CXU-5.3 i ZVI/CXM-5.3) van mostrar unes prestacions bones, arribant a més del 87% de conversió de fenol després de 60 min de CWPO. Pel contrari, l'eliminació de fenol per simple adsorció o CWPO utilitzant els mateixos materials en absència de ZVI (CXU-5.3 i CXM-5.3) van proporcionar una baixa eficiència d'eliminació, per sota del 5% després de 60 min. En conclusió, la presència de ZVI sobre catalitzadors que contenen nitrogeno rendeix una millor eliminació de fenol, que arriba a valors pel sobre del 93% després de 3 h, especialment per a aquells xerogels de carboni amb major contingut de nitrogen (ZVI/CXM-5.3 i ZVI/CXM-6.9).

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CHAPTER 1

Introduction

The first chapter of this thesis presents general considerations about water quality, mainly focusing on the industrial wastewaters containing phenol. A short description of the wastewater treatment alternatives and their limitations for the removal of phenol in water is presented, mostly dedicated to advanced oxidation processes (AOPs). A brief description of the homogeneous and heterogeneous Fenton systems is done. The role of the support on the heterogeneous Fenton process is emphasized, given special attention to the case of activated carbon and carbon xerogel. An overview of the results reported for heterogeneous wet peroxide oxidation of phenol in the literature is also provided.

1.1 Water: General considerations

Water is one natural resource that is absolutely essential for all life. Because of this, humans are always in search for clean and fresh water for their life. It is obvious that global freshwater resources are endangered due to growing demand, which resulted from rising world population and climate change. For example, according to the *Instituto Nacional de Estadística* data (INE, 2012), a continuously increasing demand of fresh water has been observed in Spain as a result of both the expanding industrialization of the country and the development of new municipal zones which is directly related to the population growth. This rising demand is hardly sustainable with the scarce water resources of the country. Furthermore, studies about the climate change foresee, a major impact in countries located in the south of Europe. It is expected that the fresh water availability in the Southern Europe will decrease by about 20% with an increase of temperature by 2 ºC. The regions that already suffer from scarce of water resources; in particular the Mediterranean Basin will experience major difficulties and costs (Stern, 2007).

This situation will get even worse when the fresh water becomes polluted. Therefore, it is very clear that the strategy to continue in the search of solutions to this problem, which is in sensitive growth, will concentrate on two fundamental aspects: the development of appropriate methods for decontamination of drinking, ground and surfaces waters, and the development of appropriate methods for wastewater treatment containing toxic or non-biodegradable compounds.

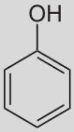
1.2 Industrial wastewaters

Wastewater can basically be divided in two major categories: urban and industrial. In the case of urban residues, the main pollutant load is mostly non toxic and biodegradable. This kind of wastewater is usually treated using biological treatment into a municipal waste water treatment plant (WWTP), which is sufficient and the most economic solution for this problem. On the contrary, industrial effluents encounter refractory and/or biotoxic compounds, which need a specific chemical treatment in order to eliminate or partly reduce their concentration to the required level allowing for direct discharge to conventional sewage plants (Matatov-Meytal et al., 1998). Examples of toxic and non-biodegradable pollutants are phenols, surfactants, chlorinated compounds, pesticides, and aromatic hydrocarbons, among many others.

1.3 Model compound for this study

Phenol is usually taken as model compound for wastewater treatment studies because it is considered as starting or intermediate compound in chemical, petrochemical and pharmaceutical industries and also formed in the oxidation pathway of high-molecular-weight aromatic hydrocarbons (Fortuny et al., 1999; Santos et.al., 2002). Table 1.1 presents the physical and chemical properties of phenol.

Table 1.1 Physical and chemical properties of phenol

Phenol	
Molecular formula	C_6H_5OH
Molar mass	94.11 g/mol
Density	1.07 g/cm^3
Melting point	40.5 ºC
Boiling point	181.7 ºC
Solubility in water	8.3 g/100mL water at 20ºC

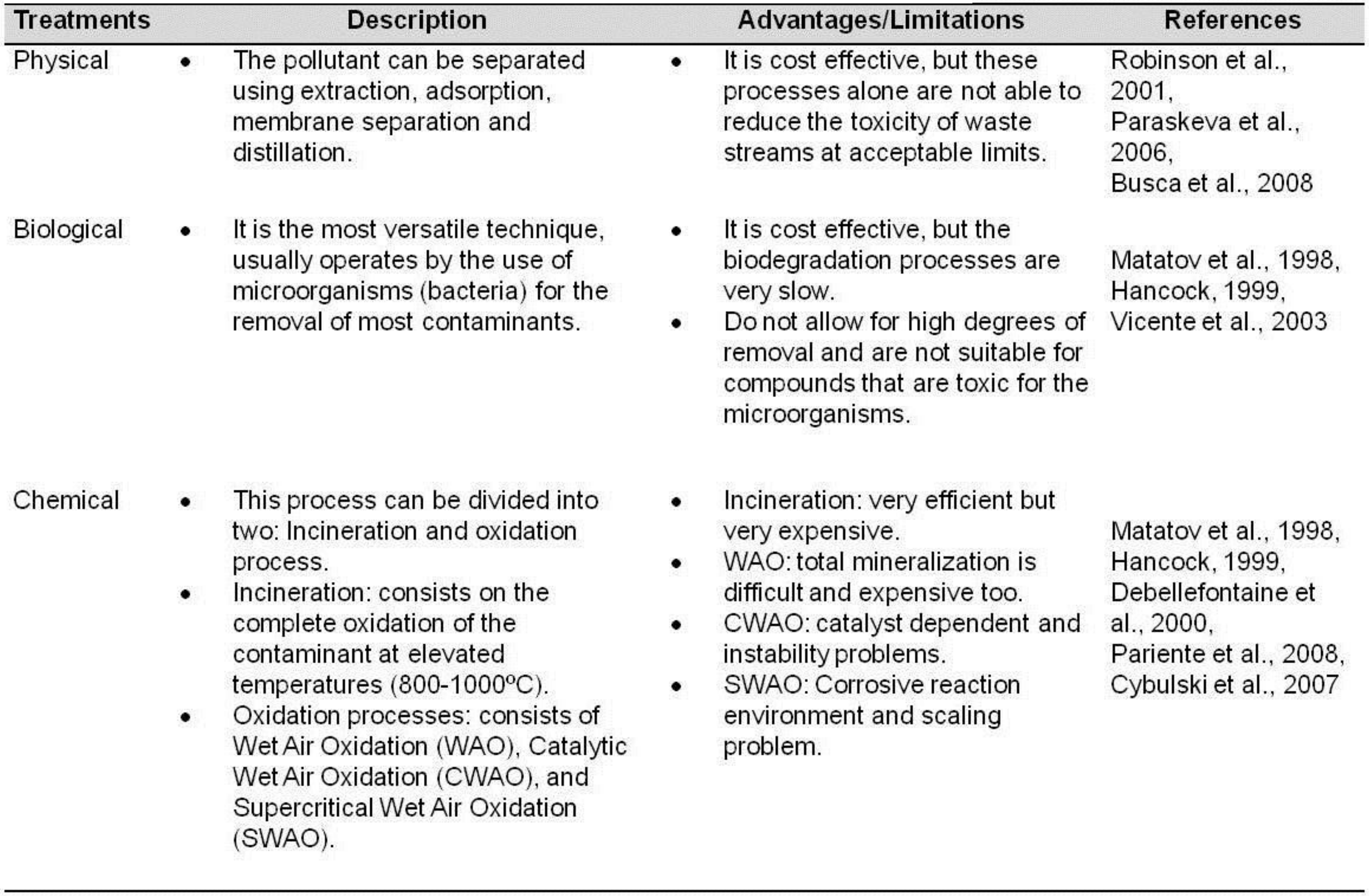
The number of synthetically produced chemical substances known is about 14 millions and it is increasing exponentially (Charpentier, 2003). The Environmental European Agency has established a list of over 2000 chemical products, which are either toxic or environmentally hazardous (EEA, 1998). Among these, phenolic and aromatic compounds (including dyes), are not only at the origin of the low biodegradability of most of the industrial effluents and besides, but also are recognized as toxic and carcinogenic to human beings (Bruce et al., 2001). Furthermore, the dye industry produces currently about 10000 different colorants among which acid and reactive colorants are the most important groups with respectively 900 and 600 species, all of them being having phenolic or aromatic structures. During 2004, almost 500 Tm of direct and over 800 Tm of indirect phenol emissions occurred in Europe (E-PRTR, 2007). It has to be pointed out that 46% of the direct emissions only took place in Spain. As released from oil, chemical paper and metal industries they are potentially capable to pollute thousands of cubic hectometers of fresh water to unacceptable levels.

1.4 Wastewater treatments alternatives

The typical processes used to decontaminate wastewaters are physical, biological and chemical treatments. Each technique has its own limitations, different applicability, effectiveness and cost. In the literature (Busca et al., 2008), the wide variety of technologies for phenol degradation from wastewater was compared. Table 1.2 summarizes the basic wastewater treatment techniques.

Summarizing, the actual conventional water and wastewater treatments have failed to response to the toxic, non-biodegradable organic pollutants, so, new improved treatment techniques have to be developed and tested in order to effectively remove these pollutants from the water sources. In this sense, Advanced Oxidation Processes (AOPs) have recently drawn a lot of attention as they can treat wastes with high total organic carbon (TOC) and chemical oxygen demand (COD) contents (Yue, 1997). AOPs are described in detail in the following section.

Table 1.2 Waste water treatment techniques description and their limitation



Treatments	Description	Advantages/Limitations	References
Physical	• The pollutant can be separated using extraction, adsorption, membrane separation and distillation.	• It is cost effective, but these processes alone are not able to reduce the toxicity of waste streams at acceptable limits.	Robinson et al., 2001, Paraskeva et al., 2006, Busca et al., 2008
Biological	• It is the most versatile technique, usually operates by the use of microorganisms (bacteria) for the removal of most contaminants.	• It is cost effective, but the biodegradation processes are very slow. • Do not allow for high degrees of removal and are not suitable for compounds that are toxic for the microorganisms.	Matatov et al., 1998, Hancock, 1999, Vicente et al., 2003
Chemical	• This process can be divided into two: Incineration and oxidation process. • Incineration: consists on the complete oxidation of the contaminant at elevated temperatures (800-1000ºC). • Oxidation processes: consists of Wet Air Oxidation (WAO), Catalytic Wet Air Oxidation (CWAO), and Supercritical Wet Air Oxidation (SWAO).	• Incineration: very efficient but very expensive. • WAO: total mineralization is difficult and expensive too. • CWAO: catalyst dependent and instability problems. • SWAO: Corrosive reaction environment and scaling problem.	Matatov et al., 1998, Hancock, 1999, Debellefontaine et al., 2000, Pariente et al., 2008, Cybulski et al., 2007

1.5 Advanced oxidation processes

In the last decades, various chemical oxidation techniques have been developed to overcome the inconveniences of conventional treatment methods, in particular for the treatment of industrial wastewaters. Among these techniques, AOPs appear to be a promising field of study, which have been reported to be effective for the degradation of soluble organic contaminants from waters, surface waters, soils and wastewaters containing non-biodegradable organic pollutants, because they can often provide an almost total degradation, under reasonably mild conditions of temperature and pressure (Hoigne and Bader, 1983a, Glaze et al., 1987; Guittoneau et al., 1988; Miller et al., 1988, Masten and Davies, 1994; Benitez et al., 1995, 1997; Casero et al., 1997; Meunier and Sorokin, 1997; Andreozzi et al., 1999)

In most of conventional AOPs, ozone, hydrogen peroxide, UV light or solid catalysts are typically used to generate hydroxyl radicals (Pera-Titus et al., 2004). Indeed, highly reactive hydroxyl radicals ($OH^{\bullet}$) are extraordinarily reactive species responsible for the destruction of pollutants (Peyton et al., 1982; Glaze et al., 1987; Glaze and Kang, 1989; Haag and Yao, 1992). Nevertheless, some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives, such as chloroform or tetrachloroethane, cannot be attacked by $OH^{\bullet}$ radicals (Bigda, 1995).

This work is specially focused on homogeneous and heterogeneous advanced oxidation process based on hydrogen peroxide, which is supposed to mainly give rise to hydroxyl radicals after catalytic decomposition, and for this reason a brief introduction of these processes is described in the next section. Hydrogen peroxide is a safe, efficient and easy to use chemical oxidant, suitable for wide usage on contamination (Elizardo, 1991), which in addition decomposes into innocuous water and oxygen. However, since hydrogen peroxide itself is not an excellent oxidant for many organic pollutants, it must be combined with UV light, salts (particularly metals) or ozone to produce the desired degradation results. One of the most promising AOPs is the Fenton process.

1.5.1 Fenton process

The Fenton reaction was discovered by H.J.H. Fenton in 1894 (Fenton, 1894). Fenton reactions involve reaction of H_2O_2 with iron ion mainly in acidic solution. Forty years later, Haber and Weiss (Haber-Weiss, 1934) discovered the oxidation mechanism which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. Fifteen years later, Barb and collaborators (Barb et al., 1949; Barb et al., 1951a;

Barb et al., 1951b) modified the reaction mechanism proposed by Haber and Weiss. Nowadays, the Fenton reaction is known to be a very efficient wastewater treatment process in the removal of many hazardous organics from water (Neyens and Baeyens, 2003) and has been used in industrial wastewater applications (Bautista et al., 2008). Because, using these Fenton reagents (i.e. hydrogen peroxide and iron) have its own advantages. Compared to the other bulk oxidants, hydrogen peroxide is relatively safe, and does not make environmental threat since it readily decomposes to water and oxygen (Jones, 1999). Likewise, iron is comparatively inexpensive, safe, and environmentally friendly and is highly abundant. Most importantly, the process can be applied at room conditions and with simple equipment (Esplugas et al., 2002; Azbar et al., 2004; Pignatello et al., 2006). Because of the remarkable success of Fenton reagent for phenol oxidation, extensive research is now focused on the exploration of different types of Fenton-like or modified systems.

1.5.1.1 Homogeneous Fenton process

As mentioned above, Fenton's reagent uses Fe ions as homogeneous catalysts, and the reagent hydrogen peroxide producing hydroxyl and perhydroxyl radicals according to reactions (1.1) and (1.2). The mechanism proposed by Barb et al. (Barb et al., 1949; Barb et al., 1951a; Barb et al., 1951b) for decomposition of H_2O_2, catalyzed by iron in acidic condition is represented by equations 1.1-1.7.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (1.1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (1.2)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (1.3)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (1.4)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + HO_2^{+} \quad (1.5)$$

$$Fe^{2+} + HO_2^{\bullet} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \quad (1.6)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (1.7)$$

From the above mechanism, the ferrous ion regeneration takes place through equation 1.2. This means that the oxidized ferrous ion (i.e. ferric ion) reacts with excess hydrogen peroxide to be reduced to the ferrous ion. The rate-limiting step in the Fenton chemistry is also represented by equation 1.2 and 1.5, as they are responsible for the regeneration of ferrous ions from the previously produced ferric ones.

The $OH^\bullet$ species produced through reaction given by Equation 1.1 will then attack the organic matter present in the reaction medium, hence the hydroxyl radical is a powerful inorganic oxidant that non-selectively reacts with numerous compounds (Walling, 1975).

The main factor influencing the Fenton processes is the solution pH. The optimum pH for the Fenton reaction has been repeatedly reported to be around 3 (Pignatello, 1992). The main reason for lower efficiency of Fenton reaction at higher pH value ($pH > 4$) is due to the precipitation of ferric oxyhydroxide or ferric hydroxide, which is not active in catalytic activity (Parsons, 2004). In this situation, less free iron ions are available to catalytically decompose hydrogen peroxide and less hydroxyl radicals are accordingly generated. Therefore, in order to achieve the optimum process efficiency, the solution pH should be controlled by the addition of a huge amount of acid. This makes the process unsuitable for many applications. As an alternative for the above drawbacks, this thesis (Chapter 3) illustrates how the addition of organic ligand (EDTA) that can complex the iron and enables the process to be carried out at neutral pH.

1.5.1.2 Heterogeneous Fenton process

Fenton processes can also be carried out under heterogeneous conditions by immobilizing the iron catalyst on a support, such as activated carbon (Lücking et al., 1998; Zazo et al., 2006; Dantas et al., 2006; Ramirez et al., 2007; Duarte et al., 2009). The main drawbacks of homogeneous Fenton process are firstly the sensitivity towards pH and, secondly, that a final separation of the soluble iron species from the treated water is needed (Hartmann et al., 2010). Neutralization and subsequent flocculation units are usually necessary prior to recovery of the active iron species in form of iron sludge. These drawbacks have promoted the development of Fenton processes based on heterogeneous catalytic systems, prepared by impregnating of iron or iron oxides into porous supports, which have been widely studied (Tachiev et al., 2000; Gemeay et al., 2003; Ishtchenko et al., 2003; Letaief et al., 2003). The most important issue in the heterogeneous Fenton process is the development of a heterogeneous catalyst with high activity and long-term stability at a reasonable cost. Among the porous solids, carbon materials have been used for long time in heterogeneous catalysis, either as direct catalysts or as a catalyst support. The detailed description for different carbon materials are stated below.

1.6 Carbon materials as catalyst supports

Carbon materials are largely used in heterogeneous catalysis, mostly in liquid phase reactions, as they can satisfy most of the desirable properties required for a suitable support, such as inertness, stability under reaction and regeneration conditions, adequate mechanical properties, diverse porous structures, or possibility to control the surface chemistry, and the cost of carbon supports is usually lower than that of the conventional supports such as alumina and silica (Rodriguez-Reinoso et al., 1987; Gurrath et al., 2000). Moreover, the advantage of carbon as a support is the stability under acidic and basic conditions, which does not apply for alumina or silica. Alumina and silica are dissolved under basic conditions, while alumina is also sensitive to acids (Roisson et al., 1987, p. 11; Stiles, 1987, p. 57).

1.6.1 Activated carbon (AC)

Activated carbons are being recognized as good adsorbents and unique materials for supporting a catalytically active phase due to the flexibility in tailoring their properties to specific needs. The adsorbent properties of AC are essentially attributed to their large surface area, a high degree of surface reactivity and favorable pore sizes. The commercially available ACs have a specific surface area of the order of 800-1500 m^2 g^{-1} (Bansal et al., 1988). This surface area is predominantly contained within micropores, which have effective diameters smaller than 2 nm, but also within mesopores with diameters between 2 and 50 nm and macropores, having diameters greater than 50 nm, according to the Dubinin classification officially accepted by the IUPAC (IUPAC, 1972). Among their many interesting applications, activated carbons have been considered over the last decades for their utilization in several processes involving heterogeneous catalytic reactions.

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 reach micropores. So, to obtain the better performance of this material, textural and chemical properties should be tuned according to the process it will be used in.

Figure 1.1 shows the internal structure of activated carbon and the different porosity in it. Depending on the molecular size of the adsorbate, it will interact with the macropore, mesopore or micropore. However, the catalytic performance can be influenced not only by the porous structure of carbon supports, but also by their surface chemical properties.

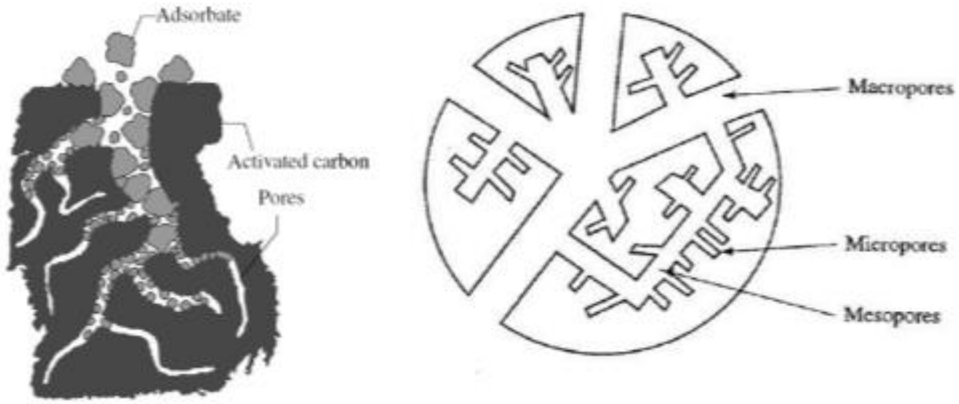


Figure 1.1 Schematic representation of activated carbon porosity (Marsh and Rodriguez-Reinoso, 2006)

Moreover, the surface chemical features of the carbon material used as support can influence the interaction with the catalyst precursor. Usually, heteroatoms, such as oxygen, hydrogen, nitrogen, hydrogen, chlorine and sulphur are present in activated carbon and other carbon materials (Rodrioguez-reinoso, 1998). These elements may be present in the starting material and become chemically bonded to the structure in the form of functional groups, during calcinations and activation steps (Rodrioguez-reinoso, 1998). Nitrogen groups are found when a nitrogen containing precursor is used, or as a result of reactions with nitrogen-containing reagents (Lahaye, 1998). Oxygenated groups are formed spontaneously by exposure of the carbon material to the ambient air. The concentration of these groups can be further increased by oxidative treatments, either in the gas (ozone, nitrous oxide, nitric oxide, carbon dioxide, oxygen, etc) or liquid (nitric acid, sodium hypochlorite, hydrogen peroxide, etc) phase (Rodrioguez-reinoso, 1998, Figueiredo and Pereira, 2010).

Figure 1.2 summarizes the different typical oxygen and nitrogen functional groups that can be found on carbon surfaces. The presence of these surface groups gives to activated carbons an acid-base character. Acidic surface oxygen groups include carboxylic acids and anhydrides, lactones or lactols, and phenols, while carbonyl and ether are neutral or may form basic structures, and the nature of quinone, chromene, and pyrone groups is still open to debate (Figueiredo and Pereira, 2010). The larger the oxygen content, the larger the hydrophilic character of the carbon surface.

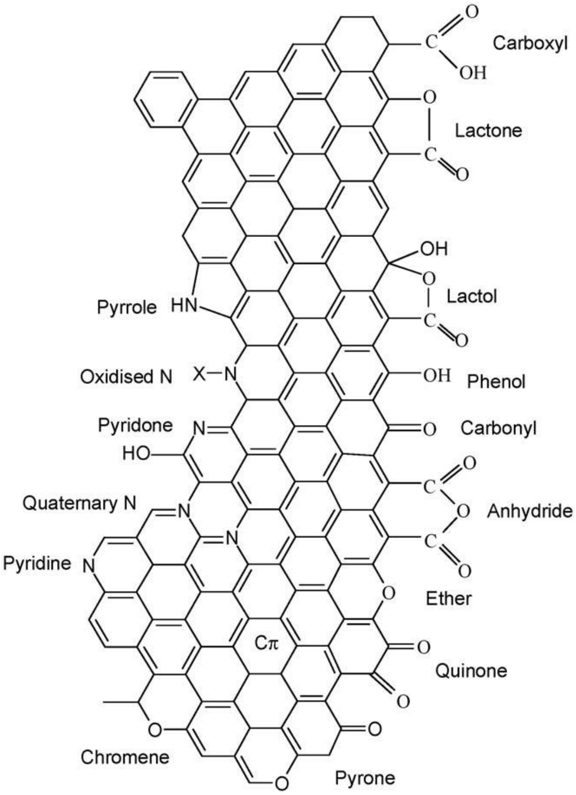


Figure 1.2 Nitrogen and oxygen surface groups on carbon (Figueiredo and Pereira, 2010)

Specific groups can be introduced or removed by selective oxidation or heat treatments. Mostly, heat treatments can be used to selectively remove some of those oxygenated groups formed, leading to an increase in the basicity of activated carbons. Figure 1.3 illustrates the temperature ranges corresponding to the evolution of CO and CO_2 upon decomposition of various types of oxygenated functional groups.

Removal of phenolic compounds by adsorption on AC has been extensively reviewed (Bansal et al., 1988) and it has been found to be function of the surface area as well as the oxygen-containing surface structures. While the presence of an acidic group decreases adsorption of phenols, the presence of carbonyl oxygen enhances the adsorption. The choice of the carbon for the removal of phenols from aqueous solutions should favor AC having large surface areas but low acidic oxygen content, such as carbon prepared at high temperatures.

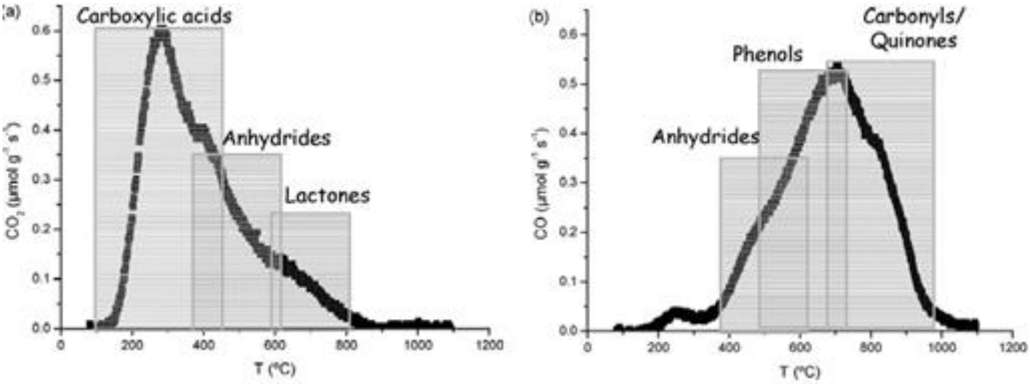


Figure 1.3 Temperature ranges corresponding to the evolution of (a) CO_2 and (b) CO upon decomposition of the various types of oxygenated functional groups (Figueiredo and Pereira, 2010)

1.6.2 Carbon Xerogel

The main advantage of these supports is that their physical properties and surface chemistry can be tailored to adapt the carbonaceous material to the catalytic requirements. Moreover, all of them present a highly mesoporous structure, diminishing diffusion problems, and both graphitic character and surface area can be conveniently modified. Comparing AC with carbon xerogel (CX), AC can be modified to some extent by chemical and thermal treatments, but their pore texture is not easily controlled and still limited (Rodriguez-Reinoso, 2008). However, CXs have emerged as a type of amorphous carbon with well controlled pore size, high purity and flexibility of the textural properties. In fact, mesoporous and macroporous textures combined with large pore volume, which is more adequate for liquid phase applications, can be obtained by this method. The key variable is the pH of the precursor solution (see Figure 1.4) (Lin and Ritter, 1997).

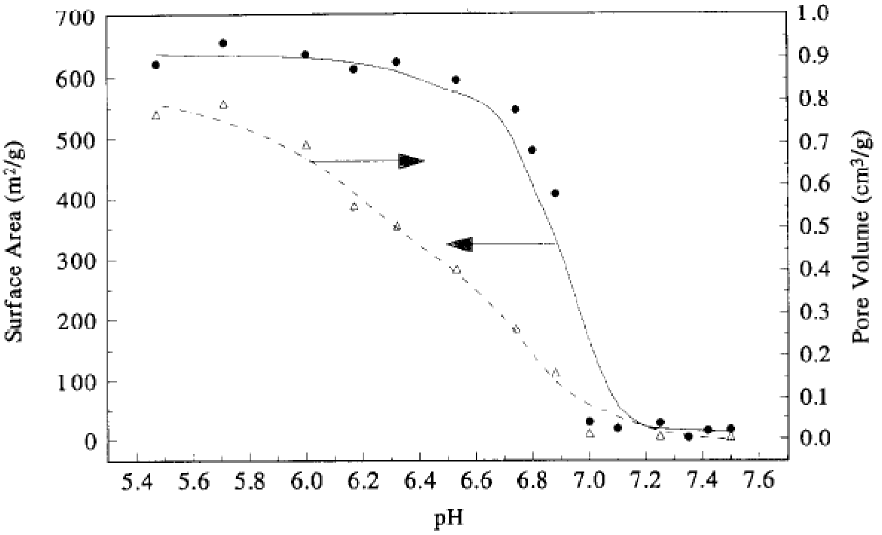


Figure 1.4 Effect of the initial pH of the resorcinol and formaldehyde solution on the surface area and pore volume of carbon xerogels (Lin and Ritter, 1997)

These materials can be obtained from the carbonization of organic gels, which are prepared by simple sol–gel polycondensation of certain organic monomers, typically resorcinol and formaldehyde. A schematic illustration of the preparation procedures of pure and N-containing carbon xerogels are presented in Figure 1.5.

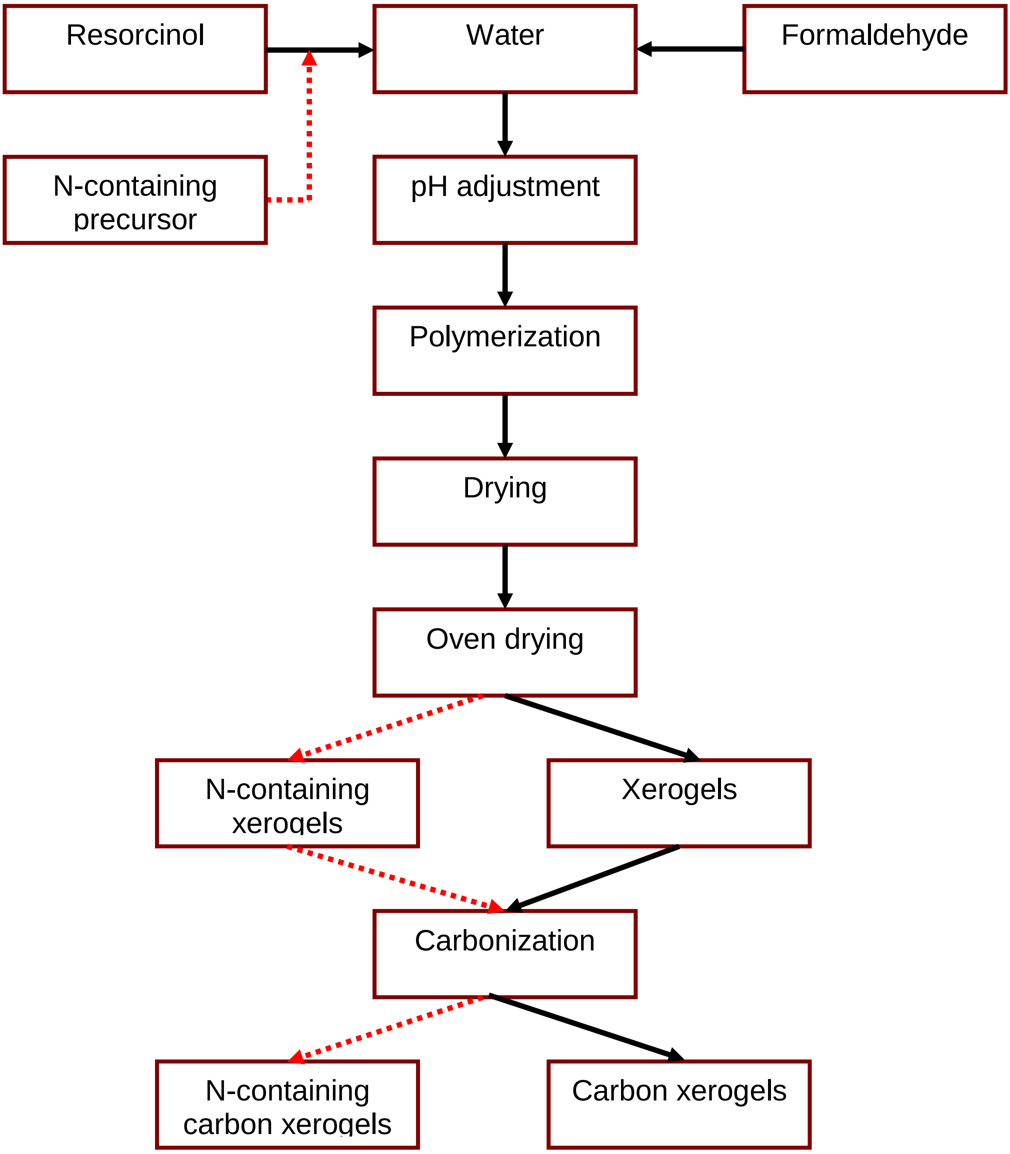


Figure 1.5 Schematic illustrations of the preparation procedures of pure and N-containing carbon xerogels

1.6.3 Carbon supported catalyst

The use of catalysts in the chemical industry is one of the major contributors to the economy of a chemical process. Most of today's chemical production processes utilize a catalytic step. In most cases the catalyst plays a key role, as it controls the activity and the selectivity of the process. Specially supported catalysts are of high interest. The typically high surface-area supports provide a good utilization of the catalytically active metal by means of high dispersion and stabilization of small metallic particles. Activated carbon supported iron catalyst has shown to be active in the degradation of phenol. For example, (Liou et al., 2010), reported that a different iron load catalyst supported on AC is active for the degradation of phenol. They observed that the effects of iron loading strongly inhibited the pore development of the catalyst but benefited the oxidation activity in WHPCO. The higher the iron contents the higher phenol conversions. Moreover, (Rey et al., 2009) have investigated the influence of different iron precursors supported on AC for the degradation of phenol in CWPO. They observed that no significant differences were observed from the iron precursors but they did not study the influence of the surface chemistry of the activated carbon.

1.7 Chelating agents

The use of chelated metals in oxidation process became in a promising technology. Chelation requires the presence of two or more atoms on the same molecule capable of metal liganding. Oxygen, nitrogen, and sulfur atoms of molecules are most commonly the metal ligands.

One of the most important group of organic compounds able to capture metal ions are aminopolycarboxylic acids e.g. Nitrilotriacetic acid (NTA), Ethylenediaminetetraacetic acid (EDTA), Ethylene Diamine Diacetic Acid (EDDA), Imino Diacetic Acid (IDA), Diethylene Triamine Pentaacetic acid (DTPA) and Hydroxyethyl Ethylene Diamine Triacetic Acid (HEDTA). These types of compounds contain several carboxylate groups linked to one or several nitrogen atoms and they are able to complex the metal ion by forming one or more stable heteroatomic rings around it. These metal complexes are stable and water-soluble and restrict the metal ions from playing their normal chemical role. As a result, chelating agents are applied in many different applications for sequestration of metal ions, to prevent metal-catalyzed reactions, for removing metal ions, or, also to increase metal availability.

Also, it is possible to obtain the benefits of using non-soluble catalysts by complexing metallic iron (which provide the iron ions) with EDTA to destroy chlorinated phenols or others phenolic compound or in the detoxification of malathion, a chemical warfare agent analogue.

On the other hand, some aminopolycarboxylic acids also represent another group of recalcitrant organic compounds and are very toxic and dangerous to humans (i.e. NTA is considered as a potential human carcinogen, however, it is extensively used as a chelating agent (Crosbie et al., 2003).

The widely used chelating agent EDTA possesses a high affinity for alkaline-earth and heavy-metal ions and forms highly stable complexes. It is thus used for many industrial purposes, where the concentrations of metal ions have to be controlled or undesirable metal contaminants have to be inactivated. For example, iron chelates of EDTA, HEDTA and NTA have been regarded as pseudocatalysts for the oxidation of HSx (Tzou et al., 2003).

In recent studies (Wang et al., 2013), ligand enhanced Fenton reaction was successfully used for the oxidation of As(III) to As(V), but As(III) oxidation was inhibited in the presence of excess EDTA at acidic and neutral pH. (Rastogi et al., 2008) also reported the effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols.

1.8 Phenol degradation: an overview

Heterogeneous catalysts based on low-valence transition metals appear as a promising alternative for the catalytic wet peroxide oxidation (CWPO) of organic pollutants since oxidation efficiencies are relatively high and pH sensitivity is lower, compared with homogeneous catalysis at the same operating conditions. Moreover, solid catalysts could be recovered by means of a simple separation step and reused. A wide variety of catalysts containing transition metal precursors supported on different materials have been tested for CWPO of phenol compounds. Main results from these previous studies are summarized in Table 1.3.

Table 1.3 Some typical results of heterogeneous wet peroxide oxidation of phenol

Catalyst	**BET surface area, $m^2\ g^{-1}$**	**Catalyst dose, $g\ L^{-1}$**	**Other reaction conditions**	**X_{PhOH}, %**	**X_{TOC}, %**	**Metal leaching**	**References**
Fe_2O_3/SBA-15 (16 wt.%)	470	0.6	Phenol 1 g/L, H_2O_2 3.8 g/L, non-controlled pH, 100ºC, 0.33 h	-	58	6%	Melero et al., 2007
Fe_2O_3/SBA-15 (10.2 wt.%)	417	1	Phenol $5*10^{-4}$ mol/L, H_2O_2 0.1 mol/L, pH 3.7, 40ºC, 4 h	100	55	11.4%	Xiang et al., 2009
CuO/activated carbon (4.6 wt.%)	670	2	Phenol 1000 mg/L, H_2O_2 , 80ºC, 3 h	100	70	-	Liou et al., 2009
CuO/Alumina	-	25	Phenol 1 g/L, H_2O_2 3.3 mL, 50ºC, 3 h	-	48	pH<4, 0.6% pH>4, 0.2%	Inchaurrondo et al., 2012
Cu/ZSM-5 (1.62 wt.%)	409	0.1	Phenol 0.01 mol/L, H_2O_2 0.1 mol/L, 60ºC, 3 h	70	-	-	Valkaj et al., 2007
Fe/Active carbon catalyst (4 wt.%)	781	0.5	Phenol 100 mg/L, H_2O_2 500 mg/L, pH 3.0, 50ºC, 4 h	100	85	10%	Zazo et al., 2006

Catalyst	BET surface area, $m^2\,g^{-1}$	Catalyst dose, $g\,L^{-1}$	Other reaction conditions	X_{PhOH}, %	X_{TOC}, %	Metal leaching	References
Fe-ZSM-5 Zeolite (2 wt.%)	-	1.5	$TOC_{[phenol]}$ 0.069 mol/L, H_2O_2 0.35 g/L, pH 3.5, 70ºC, 3 h	100	46	3.7 mg/L	Fajerwerg et al., 1996
Iron containing silicates, catalyst B (2.5 wt.%)	-	0.5	Phenol 170 mg/L,163% H_2O_2 (excess stoichiometric ratio), pH 3.5, 80ºC, 3 h	100	81	2%	Crowther et al., 2003
Fe-MMM-2 (1 wt.%)	962	1	Phenol 1mM, $H_2O_2$14 mM, pH 6.2, 60ºC, 3.5 h	100	-	<0.01	Timofeeva et al., 2007
CuNiAl3-5	89	0.01	Phenol 0.1g/L, phenol/H_2O_2 (mol): 2.0, pH 5.0, 65ºC, 2 h	63	-	-	Dubey et al., 2002
CuY-5 (4.09 wt.%)	-	0.1	Phenol 0.01 mol/L, H_2O_2 0.03 mol/L, pH 3.5-4, 70ºC, 3 h	80	-	-	Zrncevic et al., 2005
Fe-TS-1 Zeolitic material	-	0.6	$TOC_{[phenol]}$ 765 mg/L, H_2O_2 stoichiometric ratio, 100ºC, 2h	100	65	15.7%	Ovejero et al., 2001

References

Andreozzi, R.; Caprio, V.; Insola, A.; Martota, R., Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.

Azbar, N.; Yonar, T.; Kestioglu, K.; Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere 55 (2004) 35–43.

Bansal, R.C.; Donet, J-P.; Stoeckli, F., Active Carbon, Marcel Dekker, Inc. New York (1988).

Barb, W.G.; Baxendale, J.H.; George, P.; Hargrave, K.R., Reactions of ferrous and ferric ions with hydrogen peroxide, Nature 163 (1949) 692–694.

Barb, W.G.; Baxendale, J.H.; George, P.; Hargrave, K.R., Reactions of ferrous and ferric ions with hydrogen peroxide. Part I. The ferrous ion reaction, Trans. Faraday Soc. 47 (1951a) 462–500.

Barb, W.G.; Baxendale, J.H.; George, P.; Hargrave, K.R., Reactions of ferrous and ferric ions with hydrogen peroxide. Part II. The ferric ion reaction, Trans. Faraday Soc. 47 (1951b) 591–616.

Bautista, P.; Mohedano, A.F.; Casas, J.A.; Zazo, J.A.; Rodriguez, J.J., Review: An overview of the application of Fenton oxidation to industrial wastewaters treatment, J. Chem. Technol. Biotechnol. 83 (2008) 1323–1338.

Benítez, F.J.; Beltrán-Heredia, J.; Acero, J.L.; Pinilla, M.L., Ozonation kinetics of phenolic acids present in industrial wastewaters from olive oil mills, Ind. Eng. Chem. Res. 36 (1997) 638–644.

Benítez, F.J.; Beltrán-Heredia, J.; González, T.; Real, F., Photooxidation of carbofuran by a polychromatic UV irradiation without and with hydrogen peroxide, Ind. Eng. Chem. Res. 34 (1995) 4099–4105.

Bigda, R.; Consider Fenton's chemistry for wastewater treatment, Chem. Eng. Prog. 91 (1995) 62–66.

Bruce, W.; Meek, M.E.; Newhook, R., Phenol: hazard characterisation and exposure-response analysis Environ. Carcino. Ecotox. Revs. C19 (2001) 305–324.

Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L., Technologies for the removal of phenol from fluid streams: A short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.

Casero, I.; Sicilia, D.; Rubio, S.; Perez-Bendito, D., Chemical degradation of aromatic amines by Fenton's reagent, Water Res. 31 (1997) 1985–1995.

Castro I.U.; Sherrington, D.C.; Fortuny, A.; Fabregat A.; Stuber F.; Font J.; Bengoa C., Synthesis of polymer-supported copper complexes and their evaluation in catalytic phenol oxidation, Catal. Today 157 (2010) 66–70.

Charpentier, J.C., Market demand versus technological development: the future of chemical engineering, Int. J. Chem. React. Eng. 1 (2003) 1–30.

Crosbie, G.A.; Lodi, A.; McB Miller, J.H.; Skellern, G.G., The control of nitrilotriacetic acid in edetic acid and its salts by liquid chromatography, J. Pharmac. Biomedical Anal. 33 (2003) 435–440.

Crowther, N.; Larachi, F., Iron-containing silicalites for phenol catalytic wet peroxidation, Appl. Catal. B: Environ. 46 (2003) 293–305.

Cybulski, A., Catalytic wet air oxidation: are monolithic catalysts and reactors feasible?, Ind. Eng. Chem. Res. 46 (2007) 4007–4033.

Dantas, T.L.P.; Mendoça, V.A; José, H.J.; Rodrigues, A.E.; Moreira, R.F.P.M., Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon, J. Chem. Eng. 118 (2006) 77–82.

Debellefontaine, H.; Foussard, J.N., Wet air oxidation for the treatment of industrial wates. Chemical aspects, reactor design and industrial applications in Europe, Waste Manage. 20 (2000) 15–25.

Duarte, F.; Maldonado-Hódar, F.J.; Pérez-Cadenas, A.F.; Madeira, L.M.; Fenton-like degradation of azo-dye Orange II catalyzed by transition metals on carbon aerogels, Appl. Catal. B: Environ. 85 (2009) 139–147.

Dubey A.; Rives V.; Kannan, S., Catalytic hydroxylation of phenol over ternary hydrotalcites containing Cu, Ni and Al, J. Mol. Catal. A: Chem. 181 (2002) 151–160.

EEA, European Environmental Agency and United Nations Environmental Program, 1998. “Chemicals in the European Environment” http://reports.eea.europa.ea.

Elizardo, K., Fighting pollution with hydrogen peroxide. Pollution Engineering 23 (1991) 106–109.

E-PRTR, The European Pollutant Release and Transfer Register. In www.prtr.europa.eu. Last time accessed June 2012.

Esplugas, S.; Giménez, J.; Contreras, S.; Pascual, E.; Rodríguez, M., Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

Fajerwerg, K.; Debellefontaine, H., Wet oxidation of phenol by hydrogen peroxide using heterogeneous catalysis Fe-ZSM-5: a promising catalyst, Appl. Catal. B: Environ. 10 (1096) L229–L235.

Figueiredo, J.L.; Pereira, M.F.R., The role of surface chemistry in catalysis with carbons, Catal. Today 150 (2010) 2–7.

Fortuny, A.; Bengoa, C.; Font, J.; Castells, F.; Fabregat, A., Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, Catal. Today 53 (1999) 107–114.

Gemeay, A.H.; Mansour, I.A.; El-Sharkawy, R.G.; Zaki, A.B., Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine, J. Mol. Catal. A: Chem. 193 (2003) 109–120.

Glaze, W.H.; Kang, J.W., Advanced oxidation processes. Description of a kinetic model for the oxidation of hazardous materials in aqueous media with ozone and hydrogen peroxide in a semi-batch reactor, Ind. Eng. Chem. Res. 28 (1989) 1573–1580.

Glaze, W.H.; Kang, J.W.; Chapin, D.H.; The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, Ozone Sci. Eng. 9 (1987) 335–352.

Guittoneau, S.; De Laat, J.; Dore, M.; Duguet, J.P.; Bonnel, C., Comparative study of the photodegradation of aromatic compounds in water by UV and H_2O_2/UV, Environ. Technol. Lett. 9 (1988) 1115–1123.

Gurrath, M.; Kuretzky, T.; Boehm, H.P.; Okhlopkova, L.B.; Lisitsyn, A.S.; Likholobov, V.A., Palladium catalysts on activated carbon supports - Influence of reduction temperature, origin of the support and pretreatments of the carbon surface, Carbon 38 (2000) 1241–1255.

Haag, W.R.; Yao, C.C.D., Rate constants for reaction of hydroxyl radicals with several drinking water contaminants, Environ. Sci. Technol. 26 (1992) 1005–1013.

Haber, F.; Weiss, J., The catalytic decomposition of hydrogen peroxide by iron salts, J. Proc. R. Soc. London A 147 (1934) 332–351.

Hancock, F.E., Catalytic strategies for industrial water re-use, Catal. Today 53 (1999) 3–9.

Hartmann, M.; Kullmana, S.; Keller, H., Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials, J. Mater. Chem. 20 (2010) 9002–9017.

Hoigne, J.; Bader, H., Rate constants of reactions of ozone with organic and inorganic compounds in water–I, Water Res. 17 (1983) 173–183.

Hoigne, J.; Bader, H., Rate constants of reactions of ozone with organic and inorganic compounds in water–II, Water Res. 1983, 17, 185–194.

Inchaurrondo N.; Cechini, J.; Font, J.; Haure, P., Strategies for enhanced CWPO of phenol solutions, Appl. Catal. B: Environ. 111– 112 (2012) 641–648.

INE, Instituto Nacional de Estadística, INEbase - Physical variables / environment -Environmentstatistics, http://www.ine.es/en/inebmenu/mnu_medioambiente_en.htm, Last accessed the 30th of November 2012.

Ishtchenko, V.V.; Huddersman, K.D.; Vitkovskaya, R.F., Part 1, Production of a modified PAN fibrous catalyst and its optimization towards the decomposition of hydrogen peroxide, Appl. Catal. A: Gen. 242 (2003) 123–137.

IUPAC, Manual of symbols and terminology, Apendix 2, Colloid and Surface Chemistry. Pure Appl. Chem., 31 (1972) 578–638.

Jones, C.W., Applications of hydrogen peroxide and derivates, Roy. Soc. Ch.: London, (1999) pp. 264.

Khalil, L.B.; Girgis, B.S.; Tawfik, T.A.M., Decomposition of H_2O_2 on activated carbon obtained from olive stones, J. Chem. Technol. Biotechnol. 76 (2001) 1132–1140.

Lahaye, J., The chemistry of carbon surfaces, Fuel 77 (1998) 543–547.

Legrini, O.; Oliveros, E.; Braun, A.M., Photochemical processes for water treatment, Chem. Rev. 93 (1993), 671–698.

Letaief, S.; Casal, B.; Aranda, P.; Martín-Luengo, M.A.; Ruiz-Hitzky, E., Fe-containing pillared clays as catalysts for phenol hydroxylation, Appl. Clay Sci. 22 (2003) 263–277.

Lin, C.; Ritter, J.A., Effect of synthesis pH on the structure of carbon xerogels, Carbon 35 (1997) 1271–1278.

Liou, R.M.; Chen, S.H., CuO impregnated activated carbon for catalytic wet peroxide oxidation of phenol, J. Hazard. Mater. (172) 2009 498–506.

Liou, R.M.; Chen, S.H.; Huang, C.H.; Hung, M.Y.; Chang, J.S.; Lai, C.L., Wet hydrogen peroxide catalytic oxidation of phenol with FeAC (iron-embedded activated carbon) catalysts, Water Sci Technol. 61 (2010) 1489–1498.

Lucking, F.; Koser, H.; Jank, M.; Ritter, A., Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution, Water Res. 32 (1998) 2607–2614.

Maduna Valkaj, K.; Katovic, A.; Zrnčević, S., Investigation of the catalytic wet peroxide oxidation of phenol over different types of Cu/ZSM-5 catalyst, J. Hazard. Mater. 144 (2007) 663–667.

Marsh, H.; Heintz, E.A.; Rodriguez-Reinoso, F., Introduction to carbon technology; Eds; Universidad de Alicante: Alicante, Spain, 1997; p 35.

Marsh, H.; Rodríguez-Reinoso, F., Activated carbon, Elsevier Ltd. 2006.

Masten, S.J.; Davies, S.H., The use of ozonation to degrade organic contaminants in wastewaters, Environ. Sci. Technol. 28 (1994) 180–185.

Matatov-Meytal, Y.I.; Sheintuch, M., Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309–326.

Melero, J.A.; Calleja, G.; Martínez, F.; Molina, R.; Pariente, M.I., Nanocomposite Fe_2O_3/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions, J. Chem. Eng. 131 (2007) 245–256.

Meunier, B.; Sorokin, S., Oxidation of pollutants catalyzed by metallophthalocyanines, Accounts Chem. Res. 30 (1997) 470–476.

Miller, R.M.; Singer, G.M.; Rosen, J.D.; Bartha, R., Sequential degradation of chlorophenols by photolytic and microbial treatment, Environ. Sci. Technol. 22 (1988) 1215–1219.

Neyens, E.; Baeyens, J., A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98(2003) 33–50.

Ovejero, G.; Sotelo, J.L.; Martinez, F.; Melero, J.A.; Gordo, L., Wet peroxide oxidation of phenolic solutions over different iron-containing zeolitic Materials, Ind. Eng. Chem. Res.,40 (2001) 3921–3928.

Paraskeva, P.; Diamadopoulos, E., Technologies for olive mill wastewater (OMW) treatment: a review, J. Chem. Technol. Biotechnol. 81 (2006) 1475–1485.

Pariente, M.I., Tratamiento de aguas residuales industriales de baja biodegradabilidad mediante un proceso continuo de oxidacion humeda catalitica con peroxido de hidrogeno, Doctoral thesis, Universidad Rey Juan Carlos (2008).

Parsons, J., (Ed.). Advanced oxidation processes for water and wastewater treatment, IWA Publishing, London, 2004.

Pera-Titus, M.; García-Molina, V.; Baños, M.A.; Giménez, J.; Esplugas, S., Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

Peyton, G.R.; Huang, F.R.; Burleson, J.L.; Glaze, W.H., Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 1. General principles and oxidation of tetrachloroethylene, Environ. Sci. Technol. 16 (1982) 448–453.

Pignatello, J.J., Dark and photoassisted Fe^{3+}-catlysed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol., 26 (1992) 944–951.

Pignatello, J.J.; Oliveros, E.E., Mackay, A., Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Critical Rev. Environ. Sci. Technol. 36 (2006) 1–84.

Ramirez, J.H.; Maldonado-Hodar, F.J.; Perez-Cadenas, A.F.; Moreno-Castilla, C.; Costa, C.A.; Madeira, L.M., Azo-dye orange II degradation by heterogeneous Fenton- like reaction using carbon–Fe catalysts, Appl. Catal. B: Environ. 75 (2007) 312–323.

Rastogi, A.; Al-abed, S.R.; Dionysiou, D.D., Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols, Water res., 43 (2009) 684-694.

Rey, A.; Faraldos, M.; Casas, J.A.; Zazo, J.A.; Bahamonde, A.; Rodríguez, J.J., Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, Appl. Catal. B: Environ. 86 (2009) 69–77.

Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P., Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technol. 77 (2001) 247–255.

Rodríguez-Reinoso, F., The role of carbon materials in heterogeneous catalysis, Carbon 36 (1998) 159–175.

Rodríguez-Reinoso, F.; Nakagawa, Y.; Silvestre-Albero, J.; Juárez-Galán J.M.; Molina-Sabio, M., Correlation of methane uptake with microporosity and surface area of chemically activated carbons, Microp. Mesop. Mater., 115 (2008) 603–608.

Roisson, P.; Brunelle, J.P.; Nortier, P., in Stiles, A.B., Ed., Catalyst supports and supported catalysts, Butterworth, Boston, 1987, p. 11.

Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, S.; García-Ochoa, F., Route of the catalytic oxidation of phenol in aqueous phase, Appl. Catal. B: Environ. 39 (2002), 97–113.

Sotelo, J.L.; Ovejero, G.; Martinez, F.; Melero, J.A.; Milieni, A., Catalytic wet peroxide oxidation of phenolic solutions over a $LaTi_{1-x}Cu_xO_3$ perovskite catalyst, Appl. Catal. B: Environ. 47 (2004) 281–294.

Stern, N., Stern Review on the Economics of Climate Change, Office of Climate Change, (2007) UK. http://www.hm treasury.gov.uk/sternreview_index.htm

Stiles, A.B., Ed., Catalyst supports and supported catalysts, Butterworth, Boston, 1987, p. 57.

Tachiev, G.; Roth, J.A.; Bowers, A.R., Kinetics of hydrogen peroxide decomposition with complexed and free iron catalysts, Int. J. Chem. Kinet. 32 (2000) 24–35.

Timofeeva, M.N.; Melgunov, M.S.; Kholdeeva, O.A.; Malyshev, M.E.; Shmakov, A.N.; Fenelonov, V.B., Full phenol peroxide oxidation over Fe-MMM-2 catalysts with enhanced hydrothermal stability, Appl. Catal. B: Environ. 75 (2007) 290–297.

Tzou, Y.M.; Wang, M.K.; Loeppert, R.H., Effect of N-hydroxyethyl-ethylenediamine-triaceticacid (HEDTA) on Cr(VI) reduction by Fe(II), Chemosphere 51 (2003) 993–1000.

Vicente, J., PhD Thesis: Wet oxidation of phenol and tiocianate, Oviedo's university (2003).

Walling, C., Fenton's reagent revisited, Accounts Chem. Res. 8 (1975) 125–131.

Wang, Z.; Bush, R.T.; Liu, J., Arsenic(III) and iron(II) co-oxidation by oxygen and hydrogen peroxide: divergent reactions in the presence of organic ligands, Chemosphere 93 (2013) 1936-1941.

Xiang, L., Royer, S.; Zhang, H.; Tatibouët, J.M.; Barrault, J.; Valange, S., Properties of iron-based mesoporous silica for the CWPO of phenol: a comparison between impregnation and co-condensation routes, J. Hazard. Mater. 172 (2009) 1175–1184.

Yue, P.L., Oxidation reactors for water and wastewater treatment, Water Sci. Technol. 35 (1997) 189–196.

Zazo, J.A.; Casas, J.A.; Mohedano, A.F.; Rodriguez, J.J., Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst, Appl. Catal. B: Environ. 65 (2006) 261–268.

Zrnčević, S.; Gomzi, Z., CWPO: An environmental solution for pollutant removal from wastewater, Ind. Eng. Chem. Res. 44 (2005) 6110–6114.

CHAPTER 2

Hypothesis and objectives

The hypothesis, the main objectives of this work and the thesis outline are presented in this chapter.

2.1 Antecedents

The need for treating wastewater prior to its discharge to the environment requires technologies that allow dealing with those specific problems that cannot be handled via conventional biological remediation. This is the case of effluents containing refractory and frequently biotoxic organic compounds, where the elimination of the organic load is hardly to be achieved in sewage plants.

Fenton reagent (Fe/H_2O_2) has demonstrated its potential for the destruction of a wide variety of organic compounds. Moreover, it offers several advantages as the decomposition of H_2O_2 leads to harmless products. Nevertheless, the poor efficiency of H_2O_2, which partly disproportionate to H_2O and less reactive molecular oxygen, the frequent need for acidification and further neutralization, the continuous addition of iron, and the subsequent separation of the precipitated catalyst makes its application expensive.

2.2 Hypothesis

On one hand, the addition of a chelating agent is expected to improve the use of the H_2O_2 through enhancing its oxidant power, i.e., or at least preventing the iron from precipitating. Its application in ideal conditions could suppose significant savings in the quantities of peroxide and catalyst used at present.

On the other hand, the immobilization of ligands over carbon materials like activated carbon or carbon xerogel containing supported iron catalyst is suspected to form an insoluble complex to avoid the subsequent separation steps and to enhance the catalytic activity.

2.3 Objective of the thesis

The overall objective of this work is the development of a heterogeneous catalyst, which contains both the active species (i.e. ZVI) and the N-containing functional groups on the surface of carbon materials giving better catalytic performance for phenol removal by CWPO. The influence of the surface chemistry and textural properties of the carbon materials on the catalytic performance was analyzed. In order to discuss the different efficiencies observed, support and catalysts were characterized.

2.3.1 Specific objectives

In order to achieve the general objective, the following specific objectives have been drawn.

a) Investigation of the effect of adding doses of chelating agent in the classic Fenton system, Fe^{2+}/H_2O_2.

b) Preparation, characterization and reaction tests of ZVI catalysts supported over activated carbon for being applied on phenol removal using CWPO.

c) Modification, characterization and reaction tests of carbon materials functionalized with N-containing groups for being applied on phenol degradation using CWPO.

d) Preparation of ZVI catalysts supported on the modified carbon materials (prepared in objective c). Catalyst preparation, characterization, reaction tests and treated effluent characterization are included.

2.4 Thesis outline

This work is organized into eight chapters including the general introduction presented in the first chapter and the hypothesis and objectives in the second chapter. The main body of the thesis appears in the Chapters 3 to 7, based on 5 scientific papers, 2 of which already published in refereed Journals, whereas the others are under review (2) or in the last phase of preparation to be submitted for publication (1). The outline of each chapter is presented as follow:

Chapter 3 illustrates the effect of adding a chelating agent on the performance of a classical Fenton system for phenol degradation. The effect of the molar ligand to iron ratio, EDTA:Fe^{2+}, initial pH and temperature on the oxidation process was studied. This part is under review in the Journal of Water Process Engineering.

Chapter 4 reports the preparation of nanoscale zero-valent iron supported on activated carbon (nZVI/AC) and the activity test for catalytic wet peroxide oxidation (CWPO) of phenol in a batch system. The effect of the initial phenol concentration, initial pH and catalyst stability in the oxidation process was investigated. This part is under review in the Desalination and Water Treatment Journal.

In Chapter 5, activated carbon with different N-containing precursors were prepared, characterized and tested as adsorbent/catalyst for adsorption/oxidation of phenol. Moreover, these modified carbon materials served to support iron and were examined as a catalyst for CWPO. This part has been published in the Journal of Applied Catalysis B: Environmental.

Chapter 6 deals with thermally modified activated carbons with different surface chemistries as ZVI supports for catalytic wet peroxide oxidation of phenol. The influence of the surface chemistry of the activated carbon on the performance of ZVI catalyst is assessed. This part is in press in the Journal of Catalysis Today.

In Chapter 7, carbon xerogels with different pore size distribution and surface chemistry are explored as ZVI support. The influence of the textural property and surface chemistry of the support on the performance of ZVI catalysts is discussed. This part is in the last phase of preparation to be submitted for publication

Chapter 8 summarizes the main conclusions of this work. Some suggestions for further work are also presented.

CHAPTER 3

Enhanced degradation of phenol by a new Fenton-like system (Fe^{2+}/EDTA/H_2O_2) at circumneutral pH [1]

This work deals with the degradation of phenol based on the classical Fenton process, which is enhanced by the presence of chelating agents. Several iron-chelating agents such as Ethylenediaminetetraacetic acid (EDTA), Nitrylotriacetic acid (NTA), Diethylenetriamine pentaacetic acid (DTPA) and Ethylenediamine-N,N'-diacetic acid (EDDA) were explored although particular attention was given to EDTA. The effect of the molar ligand to iron ratio, EDTA:Fe^{2+}, initial pH and temperature on the oxidation process was studied. The results demonstrate that the proposed alternative approach allows extending the capacity of degrading phenol from the usual acidic pH (around 3.0) to circumneutral pH range (6.5-7.5). The overall feasibility of the process depends on the chelating agent concentration and the initial pH of the solution. The maximum phenol conversion, over 95% for a 1000 mg/L of phenol solution is achieved using 7 mg/L of Fe^{2+}, a 0.3 to 1 molar ratio of EDTA:Fe^{2+}, stoichiometric ratio of H_2O_2 (5000 mg/L), at initial pH of 7.0 and 30 ºC of temperature after 2 hours of reaction, whereas only 10% of phenol conversion is obtained without EDTA. However, in excess of ligand (EDTA:Fe^{2+} > 1), the generation of radicals seems to be strongly suppressed. Improvement on the phenol removal efficiency at neutral pH also occurs for the other chelating agents tested.

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[1] S.A. Messele, C. Bengoa, F. Stüber, A. Fortuny, A. Fabregat, J. Font, Enhanced degradation of phenol by a new Fenton-like system (Fe^{2+}/EDTA/H_2O_2) at circumneutral pH. Under review in the Journal of Water Process Engineering.

3.1 Introduction

The treatment of wastewater has increasingly become a challenge for a number of industries. In many cases, biological treatment is sufficient and the most economic solution for this problem. Nevertheless, many industrial and some urban effluents contain refractory and/or biotoxic compounds, which need a specific chemical treatment in order to eliminate or partly reduce the concentration of contaminants up to the required level allowing for direct discharge to conventional sewage plants (Matatov-Meytal et al., 1998). Examples of toxic and non-biodegradable pollutants are phenols, surfactants, chlorinated compounds, pesticides, and aromatic hydrocarbons, among many others. Phenol is usually taken as model compound for wastewater treatment studies because it is considered as starting or intermediate compound in chemical, petrochemical and pharmaceutical industries and also formed in the oxidation pathway of high-molecular-weight aromatic hydrocarbons (Santos et al., 2002 et al.,; Fortuny et al., 1999)

Most of the applied technologies to treat refractory compounds are based on expensive chemical oxidation, either because of the drastic operating conditions (CWAO), costly equipments (H_2O_2/UV) or dedicated oxidants (O_3) (Pera-Titus et al., 2004). In this regard, the well-known Fenton reagent (Fe^{2+}/H_2O_2) has shown interesting results and some significant advantages: (i) iron is a widely available and a non-toxic element, (ii) H_2O_2 is easy to handle and its decomposition leads to harmless products (Jones, 1999) and (iii) the process can be applied at room conditions and with simple equipment (Esplugas et al., 2002; Azbar et al., 2004; Pignatello et al., 2006). However, its application to the treatment of real wastewater has been so far limited mainly due to the requirements of chemicals to acidify the wastewater, which results in major operational costs. Classical Fenton-based process is restricted to an acidic pH range, the optimum pH being 3.0, due to the inability of the homogeneous iron catalyst to remain in solution at pH beyond 4.0. This means that, as the pH increases from strongly acidic to neutral, the application of Fenton's reagent to wastewater remediation is hampered by the formation of amorphous iron oxide precipitates (Pignatello et al., 2006; Duesterberg et al., 2008). This reduces the efficiency of reagents during the reaction and also generates a high amount of chemical sludge.

In this sense, addition of chelating agents in the reaction system could prevent precipitation of iron in the solution at higher pH (6.0-7.0) by forming stable chelates with iron ions, and promote its availability for hydroxyl radical generation from peroxide in a wider pH range (Tachiev et al., 2000).

Some studies have reported a quick entire destruction of chlorophenols using hydrogen peroxide activated with iron catalysts complexed with tetraamidomacrocylic ligand (TAML). This provides an efficiency of one order of magnitude higher than the classic Fenton (Collins, 2002; Gupta et al., 2002). The route has also been tested for destruction of phenolic structures (Wingate et al., 2004) and oxidation of the colorant Orange II (Chahbane et al., 2007). Moreover, it has been demonstrated that other ligands like EDTA have been widely used to enhance the efficiency of Fenton's reaction due to their strong complexing ability with multivalent cation (Sun and Pignatello, 1992; Li et al., 2007), and also capable of activating the formation of hydroxyl radical when they are added in Fenton systems (Wink et al., 1991). In addition, the capacity of the chelating ligands to activate the decomposition of the peroxides and to intensify the generation of radicals has been widely confirmed (Bull et al., 1983). Even though there are different studies that deal how to overcome the drawbacks of the Fenton reaction, there is a lack of systematic investigation about the effect of different operational parameters and the possibilities of the addition of different ligands on the oxidation of phenol by Fenton process. Therefore, a comparison study in the oxidation of phenol under acidic and basic initial pH conditions was accomplished using different EDTA:Fe^{2+} molar ratios. Furthermore, decomposition rate of H_2O_2 during the reaction, effect of other iron-chelating agents, effect of iron concentration and temperature were also investigated.

3.2 Materials and methods

3.2.2 Chemicals

Phenol (PhOH), used as major model compound, was purchased from Panreac (>99% purity, ref. 144852, C_6H_6O). Fenton reagents, hydrogen peroxide (H_2O_2 30% w/v solution, ref. 211076) and Iron(II) sulphate heptahydrated (>98% purity, ref. 131362, $FeSO_4 \cdot 7H_2O$) were also purchased from Panreac. The chelating agents used in this study were: Ethylenediaminetetraacetic acid disodium salt dihydrate (98% purity, ref. 14669, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) purchased from Panreac; Nitrilotriacetic acid trisodium salt (98% purity, ref. N0253, $C_6H_6NO_6Na_3$) supplied by Sigma; Diethylentriamine pentaacetic acid (≥98% purity, ref. 32320, $C_{14}H_{19}N_3O_{10}$); and Ethylenediamine diacetic Acid (≥98% purity, ref. 03575, $C_6H_{12}N_2O_4$) obtained from Fluka. Sulphuric acid (95-97% purity, ref. 258105, H_2SO_4), and sodium hydroxide (98% purity, ref. S8045, NaOH) were purchased from Aldrich, these reagents were used to adjust the initial pH values. Deionised water was used to prepare all the aqueous solutions.

3.2.3 Experimental set-up and procedure

A magnetically stirred jacketed reactor was used for all oxidation reactions. The reactor has a 200 mL capacity. The reaction temperature was set and controlled by circulating deionised water from a thermostatic bath through a jacket.

The reactor was filled with 100 mL of solution containing 1000 mg/L of phenol, 7 mg/L of Fe^{2+}, and a variable concentration of EDTA, selected to give the desired EDTA:Fe^{2+} ratio (0:1, 0.3:1, 0.5:1, 1:1, and 2:1). The pH was adjusted by adding NaOH or H_2SO_4. Once the desired temperature was reached (30 ºC), a small volume (1.7 mL) of concentrated hydrogen peroxide was added to provide the stoichiometric amount of H_2O_2 (5000 mg/L) and to start the reaction. All the experiments were carried out at a stirring rate of 300 rpm and for 2 hours.

During the reaction, 1 mL samples were withdrawn at 0, 3, 5, 10, 15, 30, 60, 90 and 120 min. Each sample was immediately quenched by using 40 µL of NaOH 6 N to stop the Fenton reaction. Then, it was filtered with a syringe filter of 0.45 µm nylon (Teknokroma, ref.TR-200101) and placed in a glass vial (Agilent) for immediate analysis. Some experiments were conducted three times to check the reproducibility of the results. The experimental error was within ±4%.

The main parameter used to compare the results in the discussion section is the conversion of phenol, X_{PhOH} defined as:

$$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \qquad (3.1)$$

where $[PhOH]_0$ is the initial concentration and $[PhOH]_t$ is the concentration at time t.

3.2.4 Analytical methods

The concentration of phenol was determined by HPLC (Agilent Technologies, model 1220 Infinity LC) equipped with a C18 reverse phase column (Hypersil ODS, 5µm, 25 x 0.4 cm from Agilent technologies). The analyses were performed with a mobile phase of a 40/60% mixture of methanol and ultrapure water (Milli-Q water) at a flow rate of 1 mL/min). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL of sample.

The Total Organic Carbon (TOC) was measured in a TC Multi Analyzer 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector. The Non-Purgeable Organic Carbon (NPOC) Combustion infrared standard method 5310B (Clesceri et al., 1989) was used. TOC was performed by chemical oxidation of the sample in a high temperature furnace (800 ºC) in presence of a platinum catalyst. The carbon dioxide produced during the oxidation was quantitatively determined by means of an infrared spectrophotometer detector. Sample acidification and aeration prior to analysis eliminate inorganic carbon.

The TOC conversion, X_{TOC}, was defined as:

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \tag{3.2}$$

$$\mathrm{TOC}_0 = \mathrm{TOC}_{(\mathrm{PhOH})0} + \mathrm{TOC}_{(\mathrm{EDTA})0} \tag{3.3}$$

where TOC_0 is the initial total TOC according to Eq. (3); $TOC_{(PhOH)0}$, the initial phenol TOC; $TOC_{(EDTA)0}$, the initial EDTA TOC; and TOC_t , the total TOC at time t.

3.3 Results and discussion

3.3.1 Effect of Ligand to Metal (L:M) molar ratio

The effect of EDTA:Fe^{2+} molar ratio was investigated in the range from 0 to 2 in order to determine the optimum conditions for best phenol removal at initial phenol concentration of 1000 mg/L and 7 mg/L of Fe^{2+} for 2 hours at pH 3.0. The results are illustrated in Figure 3.1a. Similar phenol conversion (95%) was obtained for the free iron catalyst and for the Fe^{2+}-EDTA complexes in the range from 0 to 1 of L:M molar ratio after 2 hours of reaction. This implies that no improvement was obtained in acidic conditions due to the addition of EDTA. It is important to note that L:M molar ratios beyond 1:1 inhibited the oxidation of phenol. This fact can be related with the degradation of EDTA with H_2O_2 in presence of different catalysts (Sillanpää et al., 2009; Kunz et al., 2002). Thus, the presence of excess EDTA does not improve the catalytic behaviour; rather it may inhibit the generation of radicals. It has already been reported that the ratio of ligand to metal is of significant importance since the generation of radicals can be reduced in the presence of excess ligand, (Rämö and Sillanpää et al., 2001; Engelmann et al., 2003; Sharma et al., 2004).

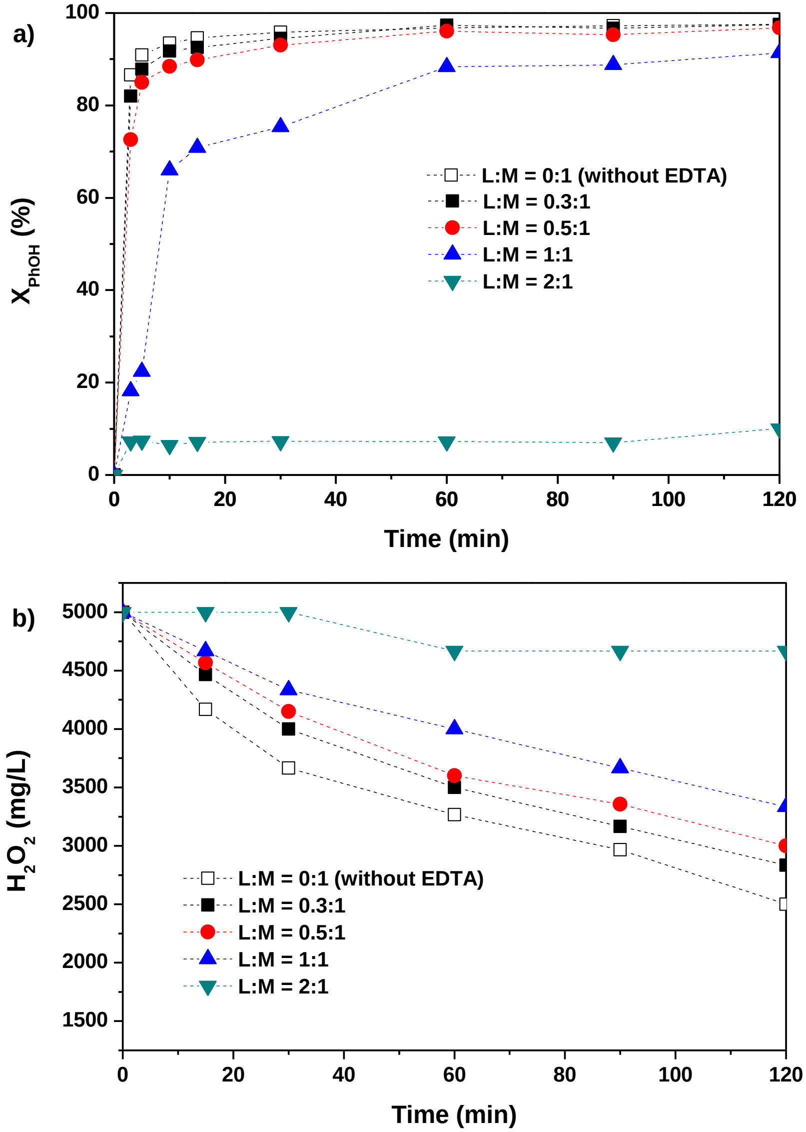


Figure 3.1 a) Phenol b) H_2O_2 conversion versus time for different EDTA:Fe^{2+} molar ratio. [Phenol] = 1000 mg/L, [H_2O_2] = 5000 mg/L, $[Fe^{2+}]_0$ = 7 mg/L , T = 30 ºC, $[pH]_0$ = 3.0, and t = 120 min.

Figure 3.1b shows the consumption of hydrogen peroxide for different L:M molar ratio at pH 3.0 in the absence of phenol. At higher ligand concentration, hydrogen peroxide decomposition rate was negligible. Therefore, it shows the same tendency as the phenol removal efficiency which depends on the L:M ratio.

3.3.2 Speciation of Fe^{2+} and Fe^{3+} in the presence of EDTA

It is well-known that Fe and EDTA in solution form a diversity of species, which distribution depends on the pH to a great extent. However, this speciation not only depends on the pH, but also on the complex formation kinetics (Walling wt al., 1970; Nowack and Sigg, 1997), and the probability of EDTA degradation when exposed to H_2O_2 (Pierce et al., 2007). The speciation diagrams of both Fe^{2+} and Fe^{3+} with EDTA as a function of pH were obtained using the thermodynamic data from the MINTEQA2 (Allison et al., 1991) database, and are shown in Figure 3.2 for an overall iron concentration range from 0 to 0.125 mM.

As it can be seen from Figure 3.2a, Fe^{2+} precipitates in the form of hydroxides at pH above 4.0. However, both Fe^{2+} and Fe^{3+} form stable complexes in the presence of strong complex forming agents like EDTA in a wide pH range, pH up to 11 (Pignatello et al., 2006). Also DTPA, EDDA and NTA give similar behavior (diagrams not shown).

Furthermore, this distribution diagram shows that Fe^{3+}-EDTA is the predominant species at a pH range of 2.0–7.0, whereas Fe^{2+}-EDTA is the major species in the range of 3.0–9.0. Based on the speciation distribution in Figure 3.2b, pH range was divided into three regions, i.e. low pH ($pH < 3.0$, Region I), mid pH ($3.0 < pH < 7.0$, Region II) and high pH ($pH > 7.0$, Region III). The speciation in the low pH range contains protonated $Fe^{2+}/^{3+}$-EDTA complexes and free Fe^{2+}, whereas, the high pH range contains the hydroxyl complexes. The above experiments were conducted at pH 3.0, so there was already highly active free Fe^{2+} and there was no possibility for Fe^{3+} to form insoluble precipitate. Therefore, the presence of EDTA does not modify the conditions of the classical Fenton, hence the nil effect of the EDTA. However, at higher pH, where Fe^{3+} precipitation in the form of hydroxide occurs, the addition of EDTA should play a relevant role. Thus, mid pH, where the Fe^{2+}-EDTA and Fe^{3+}-EDTA are predominant species, was chosen for the subsequent experiments.

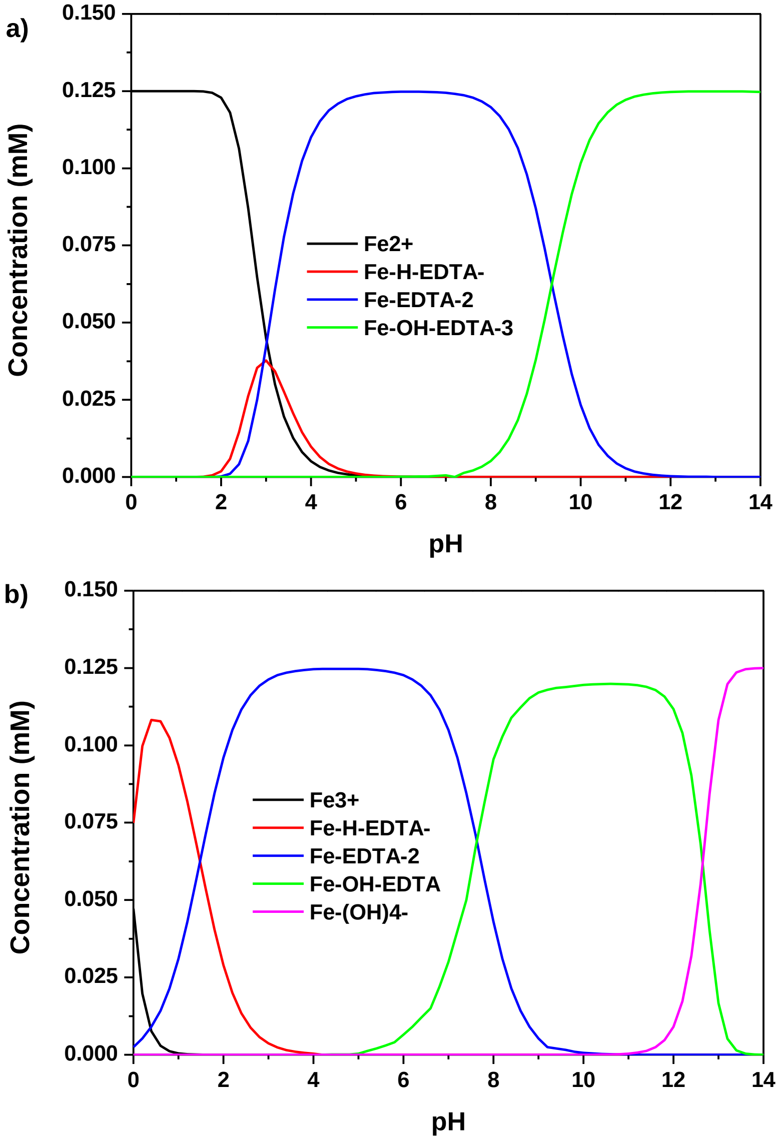


Figure 3.2 Equilibrium distribution of [Fe-EDTA] species as a function of pH for (a) Fe^{2+} and (b) Fe^{3+}, assuming 0.125 mM concentration of Fe and EDTA. (from MINTEQ software (Allison et al., 1991))

3.3.3 Effect of initial pH

Considering the Fe-EDTA species diagrams, different initial pHs were evaluated in order to explore the effect of pH over the Fenton process in the presence of EDTA. As it can be seen in Figure 3.3b, only small performance changes were noted again for acidic conditions (pH 3.0 and 5.0) in the presence of EDTA (0.3:1 L:M ratio, i.e. 0.125 mM Fe^{2+}) compared to the equivalent free Fe^{2+} catalyst (Figure 3.3a), reaching a final 95% phenol conversion with both Fe^{2+} and Fe^{2+}-EDTA.

However, under circumneutral conditions (pH 6.5-7.0), the addition of EDTA brings to phenol conversion over 95% (Figure 3.3b). It is important to note that the conversion at circumneutral pH without EDTA only reaches 10% of phenol conversion (Figure 3.3a). As expected, at pH above 4–5 without EDTA, the reaction does not proceed because of the iron precipitation. Moreover, Figure 3.3a and Figure 3.3b respectively show that at higher pH, e.g. 8.0, the conversion drops again both in the absence and presence of EDTA. For instance, under the same operating conditions, only 10% was achieved in the absence of EDTA and 35% in the presence of EDTA. The decrease in the reaction rates at pH 8.0 can be due to changes in the speciation of Fe^{3+} towards hydroxide complex species, which are probably not active for the generation of radicals and suppress the catalytic properties of iron. In addition, hydrogen peroxide stability is also strongly affected by pH conditions (Szpyrkowicz et al., 2001). Thus, a further increase of the pH above neutral values results in favouring the H_2O_2 decomposition into water and molecular oxygen (Lin and Chen, 1997).

Figure 3.4 shows the pH evolution, phenol and TOC conversion versus time for different L:M ratios under the same experimental conditions but at initial pH solution of 7.0. The result illustrates that the feasibility of the process mainly depends on both the chelating agent concentration used to promote the reaction and the initial pH of the solution. This means that, the presence of EDTA resulted in increased iron solubility at higher pH. Consequently, the Fenton reaction can be conducted over a broader range of pH when iron is complexed with EDTA.

Figure 3.4a shows the degradation rate of phenol for each, EDTA:Fe^{2+} ratio, which increased in the order 0.3:1 > 0.5:1 > 1:1. However, in excess of ligand (EDTA:Fe^{2+} >1), only 10% of phenol conversion was achieved, because the presence of excess EDTA inhibited the generation of radicals, and this strongly reduces the efficiency of phenol removal. Overall, the presence of EDTA highly increased the pH range where the classical Fenton system is feasible, which results in major cost savings as this eliminates the need for initial acidification.

Enhanced TOC removal was also observed during the oxidation. As it can be seen in Figure 3.4b, the TOC reduction was 4.7%, 20.1%, 19.0%, 16.6% and 0.6% for L:M ratio of 0:1, 0.3:1, 0.5:1, 1:1 and 2:1, respectively, after 2 hours of reaction. From the results, it can be seen that the amount of ligand also has a great effect on phenol total mineralization. Thus, the phenol and TOC conversion at initial pH of 7.0, in the absence (0:1) and excess (2:1) of EDTA is insignificant. However, the addition of small amounts of EDTA in the range of 0.3:1 to 1:1 EDTA:Fe^{2+} ratio shows a significant improvement on the degradation.

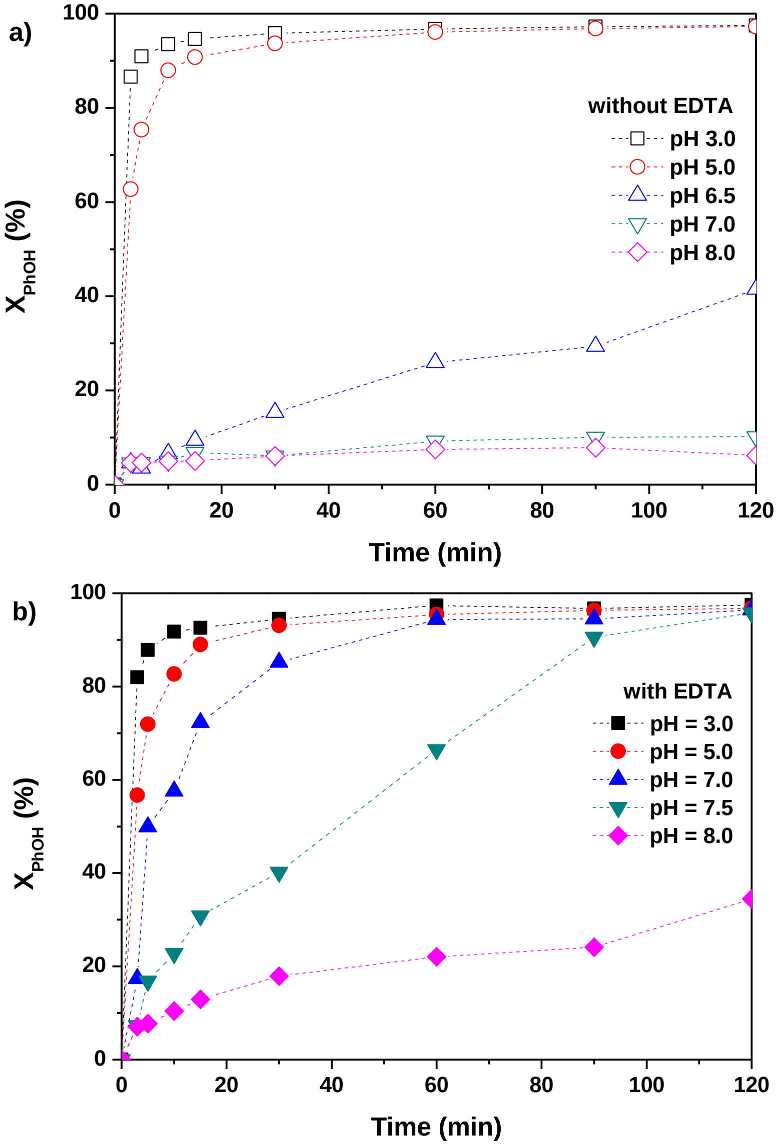


Figure 3.3 Phenol conversion versus time for different initial pH solution. [Phenol] = 1000 mg/L, $[H_2O_2]$ = 5000 mg/L, $[Fe^{2+}]_0$ = 7 mg/L, T = 30 ºC, and t = 120 min. a) without EDTA (L:M = 0:1) b) with EDTA (L:M = 0.3:1)

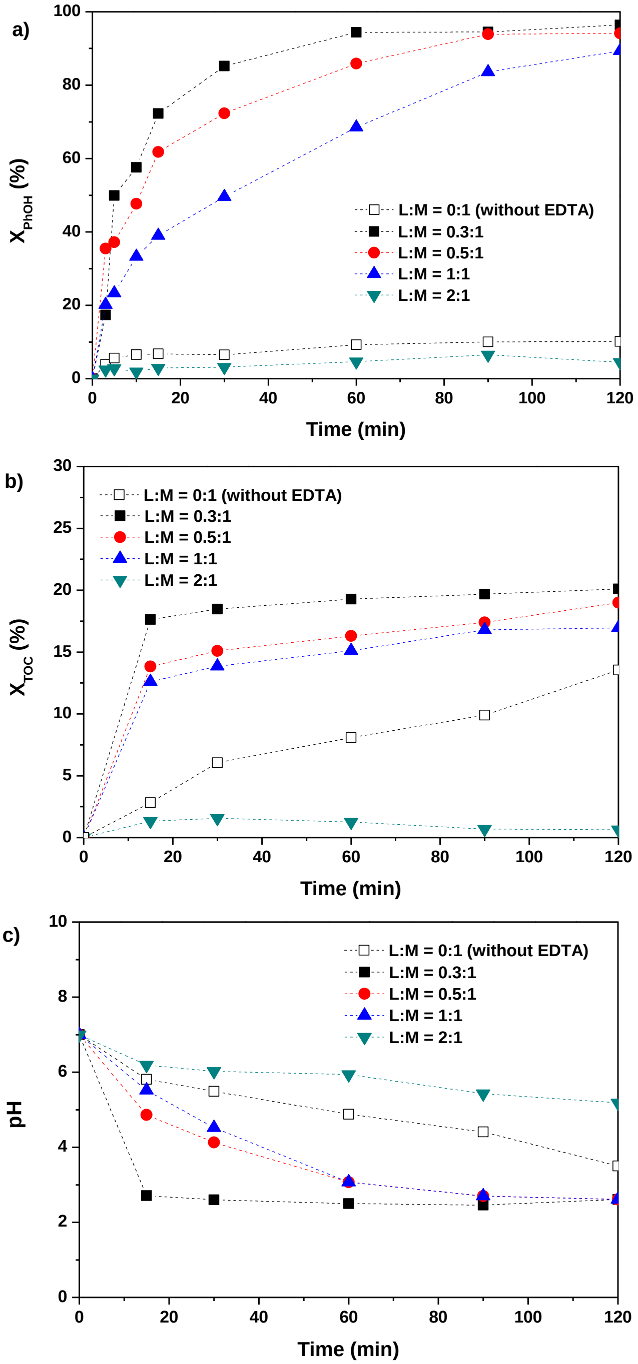


Figure 3.4 a) Phenol conversion b) TOC conversion and c) pH evolution versus time for different EDTA:Fe^{2+} molar ratio. [Phenol] = 1000 mg/L, [H_2O_2] = 5000 mg/L, [Fe^{2+}]$_0$ = 7 mg/L , T = 30 ºC, [pH]$_0$ = 7.0, and t = 120 min

Figure 3.4c illustrates the pH variation of the solution during the reaction. After starting the reaction, the pH of the solution decreases dramatically in the first 15 min from original pH 7.0 to pH 5.8, 2.7, 4.9, 5.5 and 6.2 for L:M ratio of 0:1, 0.3:1, 0.5:1, 1:1 and 2:1, respectively. During the reaction, the decrease of the pH of the solution is very significant for the EDTA:Fe^{2+} ratio of 0.3:1, 0.5:1, 1:1, which agrees with the formation of low molecular weight acid intermediates. For the EDTA:Fe^{2+} ratio of 0.3:1, the solution pH arrives to a plateau after 30 min of reaction. In this experiment, the best results were obtained using 0.3:1 EDTA:Fe^{2+} molar ratio (Figure 3.4), reaching over 95 % of phenol and 20.1% TOC conversion under neutral pH. Subsequently, the EDTA:Fe^{2+} ratio was set at 0.3:1 in the following experiments.

3.3.4 Effect of temperature and iron concentration

The influence of two temperatures (30º C and 60º C) and two iron concentrations (7 mg/L and 28 mg/L) on the oxidation of phenol was studied in the presence of EDTA using the optimal EDTA:Fe^{2+}molar ratio previously found, i.e. 0.3:1, and without EDTA (0:1), in all cases the initial pH of the solution was at pH 7.0. Figure 3.5a clearly demonstrates that an increase in the iron concentration and temperature favours the phenol degradation. The phenol degradation profile obtained in the presence of EDTA at 30 ºC and 7 mg/L of iron showed that, even at the lower temperature, 96% of phenol disappears after 2 hours of reaction. As expected, a higher temperature and iron concentration led to the increase of the reaction rate. At 60 ºC and 7 mg/L of iron, the same conversion of 96% was found after only 60 min and the conversion was complete in just 30 min when 28 mg/L of iron were applied at 30 ºC. Interestingly, without EDTA (L:M = 0:1), the results obtained for the phenol removal indicated a maximum phenol conversion of 10% and 36% for 7 mg/L of iron at 30 and 60 ºC, respectively, whereas, at 30 ºC and 28 mg/L of iron, the conversion was 58%. This confirms that, at neutral pH, the presence of EDTA plays a major role. For instance, the addition of EDTA at one-third of the molar stoichiometric ratio with respect to the iron is able to increase the phenol conversion from 10% to 96% at 30 ºC and 7 mg/L of iron; this is almost ten times higher.

Figure 3.5b shows the hydrogen peroxide consumption at the two different temperatures and iron concentrations in the presence of EDTA using EDTA:Fe^{2+} molar ratio of 0.3:1 and without EDTA (0:1), in all the cases the initial pH of the solution was 7.0. At higher temperature and iron concentration, hydrogen peroxide decomposition rate also improved. Accordingly, phenol removal efficiency shows the same tendency as the peroxide decomposition rate and also small values of hydrogen peroxide conversion were encountered for the systems without EDTA at pH 7.0, even at higher temperature and iron concentration.

This trend was already reported in the literature for different cases. Walling (Walling, 1975) and Oakes and Smith (Oakes and Smith, 1983) confirmed that while Fenton's reaction is effective in many cases, Fe^{2+} catalyzed hydrogen peroxide decomposition rate takes feasible values only in a narrow pH range (3-4) where the activity is significant. However, it has also been reported that complexed forms of iron are active for hydrogen peroxide decomposition over a much wider pH range (Francis et al., 1985).

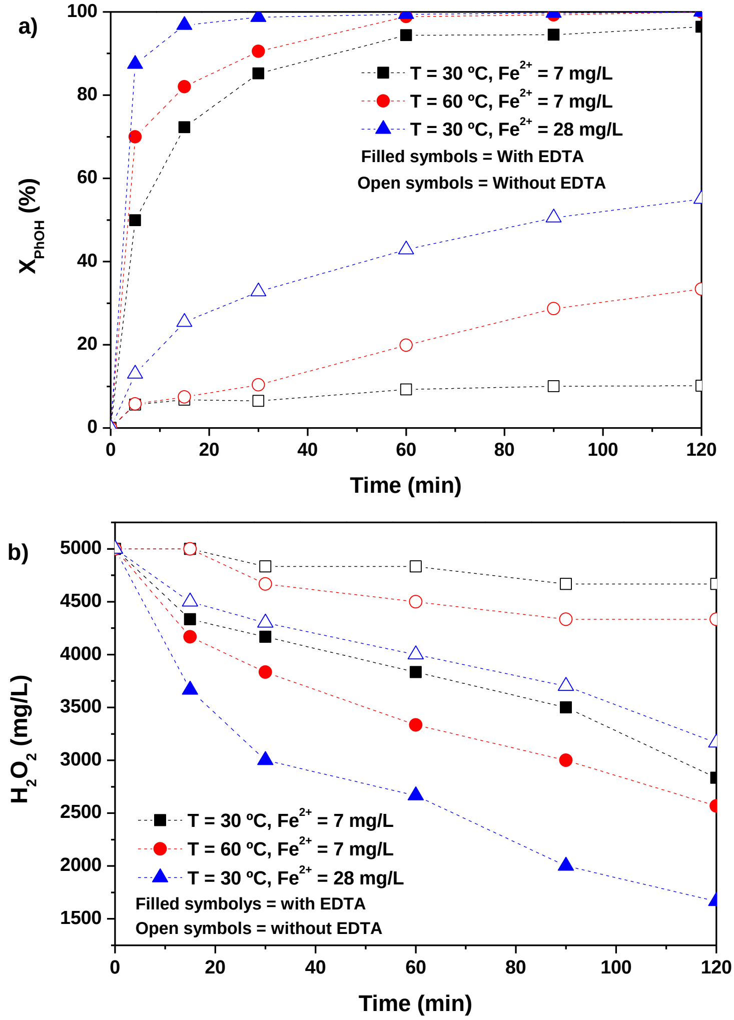


Figure 3.5 Effect of temperature and Fe concentration on a) Phenol and b) H_2O_2 conversion. [Phenol] = 1000 mg/L, $[H_2O_2]$ = 5000 mg/L, $[pH]_0$ = 7.0, L:M = 0.3:1, and t = 120 min

There are several studies on the reaction between hydrogen peroxide and free or complexed iron ions in aqueous solution. Two different reaction mechanisms have been proposed. The first reaction pathway considers the generation of radicals through a classical set of reactions as proposed by Haber and Weiss (Haber and Weiss, 1934).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (3.4)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad (3.5)$$

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^{+} \quad (3.6)$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \quad (3.7)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \quad (3.8)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \quad (3.9)$$

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (3.10)$$

In the presence of a radical scavenger, e.g. some organic compound, the radicals can attack it and this alternative pathway can compete, often favourably, with the self-decomposition of the hydrogen peroxide into water and oxygen (Neyens and Baeyens, 2003). If Fe^{3+} is removed from the system, Fe^{2+} is progressively exhausted and the reaction stops, which occurs when the pH is not acidic enough for preventing the formation of inactive, insoluble $Fe(OH)_3$. Hence, the main role of the EDTA seems to be maintaining Fe^{3+} in solution even at neutral pH, without negatively impacting the rest of steps.

Although other researchers have alternatively suggested the intermediate generation of highly reactive ferryl ion (Fe^{4+}) (Barb et al., 1951; Rahhal and Ritcher, 1988; Rush et al., 1990) and, in spite of their fundamental differences, the two schemes are surprisingly hard to distinguish. Rahhal and Ritcher (Rahhal and Ritcher, 1988) suggested that the pH of the system is the determining factor as to whether hydroxyl radicals or ferryl ions are generated.

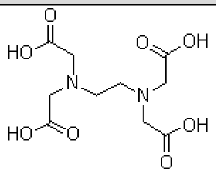
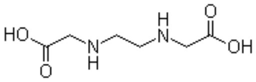
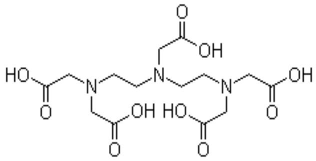
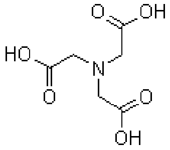
Therefore, from our results, the addition of EDTA in the Fenton system indeed leads to a more efficient consumption of H_2O_2, which indicates an enhanced iron-catalyzed H_2O_2 decomposition into radicals and, in accordance, an improved phenol removal rate. In conclusion, this can be considered as an intensification of the conventional Fenton process.

3.3.5 Effect of the chelating agent

To study the effect of the chelating agent over this oxidation process, four different chelating species were tested (EDTA, EDDA, DTPA and NTA).

These compounds were used in this study because they are commercially available, similar in structure and represent a potentially useful class of Fe^{2+}/Fe^{3+} chelate catalysts. Table 3.1 shows the structures of these compounds.

Table 3.1 Formula and structure of the different chelating agents tested

Compound	**Schematic structure**	**Molecular Formula**	**Molecular Weight (g/mol)**
Ethylenediaminetetraacetic acid (EDTA)		$C_{10}H_{16}N_2O_8$	292.24
Ethylenediamine-N,N'-diacetic acid (EDDA)		$C_6H_{12}N_2O_4$	176.17
Diethylenetriamine pentaacetic acid (DTPA)		$C_{14}H_{23}N_3O_{10}$	393.35
Nitrilotriacetic acid (NTA)		$C_6H_9NO_6$	191.14

The tests were carried out for each chelating agent, with L:M ratio of 0.3:1 (except NTA 0.6:1, as NTA is tridentated) (Tachiev et al., 2000), 7 mg/L of iron concentration, an initial concentration of phenol of 1000 mg/L, stoichiometric ratio of H_2O_2, at initial pH solution of 7.0 and 30 ºC of temperature.

As it can be seen in Figure 3.6, the phenol degradation markedly depends on the chelating agent used for enhancing the oxidation. At 30 min of reaction, in terms of phenol conversion, the reactivity order observed was EDDA (93%) > EDTA (85%) > DTPA (81%) > NTA (63%). However, quite similar conversions (96%) were obtained for all chelating agents after 60 min of reaction. These results could be due to the fact that the stability of Fe^{2+} complex formed with each chelating agent could follow the speciation of Fe^{2+}, thus avoiding precipitation of iron at higher pH as suggested for EDTA. The pH evolution (data not shown) exhibits almost the same values, a minimum value (2.5) at approximately 120 min for all chelating agents, again suggesting the formation of organic acids.

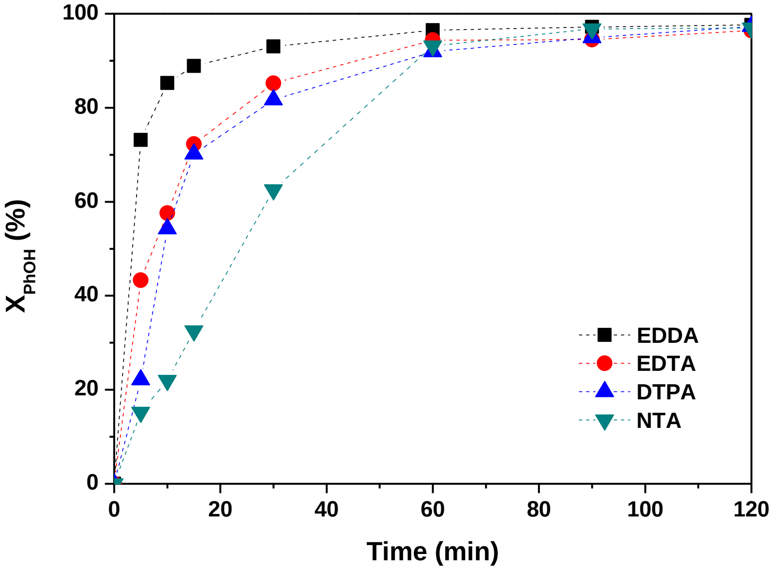


Figure 3.6 Phenol conversion for different chelating agent. [Phenol] = 1000 mg/L, $[H_2O_2]$ = 5000 mg/L, $[Fe^{2+}]0$ = 7 mg/L , T = 30 ºC, $[pH]_0$ = 7.0, L:M =0.3:1, and t = 120 min

Although the main role of the chelating agent is believed that prevents the formation of $Fe(OH)_3$, the complex formed must somehow modify the reaction steps where Fe^{3+} participates, particularly in Eq. 3.6, where it is reduced back to Fe^{2+} allowing continuing the generation of oxyradicals from the hydrogen peroxide. This reaction is the slowest and often is the rate controlling step for the overall process. Therefore, a too stable Fe(III)-chelant complex may slow down this step. From this point of view, EDDA seems to possess a structure less favourable to form a very stable complex so the reduction of the Fe^{3+} is facilitated, yet it is able to keep it in solution.

3.4 Conclusions

Aqueous phase oxidation of phenol solutions (1000 mg/L) has been conducted from acidic up to circumneutral pH using classical Fenton system (Fe^{2+}/H_2O_2) with or without the addition of a chelating agent in order to enhance the oxidation performance. EDTA was selected for most of the tests under the same Fe^{2+} catalyst load (7 mg/L) and H_2O_2 dose (stoichiometric with respect to phenol).

In acidic conditions, close to the optimal pH (3-4), the presence of EDTA does not change the phenol conversion achieved under classical Fenton conditions, but, in excess of EDTA the phenol conversion becomes insignificant.

The phenol removal efficiency and peroxide decomposition rate significantly improved in presence of EDTA at near circumneutral pH. Over 95% of phenol conversion was obtained using an EDTA: Fe^{2+} ratio of 0.3:1 at pH 7.0, which is almost tenfold of that being obtained in the absence of EDTA. Among the different EDTA: Fe^{2+} molar ratio tested, 0.3:1 ratio was found to be the optimum.

Other chelating agents, like EDDA, DTPA and NTA, were also tested in this study. All they demonstrated to enhance the oxidation ability of the Fenton system at neutral pH although EDDA provided the best oxidation performance.

Overall, the presence of a chelating agent in small quantities greatly broadens the pH range where the Fenton-like system is feasible, up to circumneutral pH. Thus, pH adjustment would not be required or just limited for many caustic real wastewaters, which can result in major saving of operational costs.

References

Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J., MINTEQA2/PRODEFA2-A Geochemical model for environmental systems, USEPA, Athens, GA (1991) EPA/600/3– 91/021.

Azbar, N.; Yonar, T.; Kestioglu, K., Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere 55 (2004) 35–43.

Barb, W.G.; Baxendale, J.H.; George, P.; Hargrave, K.R., Reactions of ferrous and ferric ions with hydrogen peroxide, Trans Faraday Soc. 47 (1951) 462–500.

Bull, C.; G. J. McClune, J. A. Fee, The mechanism of Fe-EDTA catalyzed superoxide dismutation, J. Am. Chem. Soc. 105 (1983) 5290–5300.

Chahbane, N.; Popescu, D.; Mitchell, D.A.; Chanda, A.; Lenoir, D.; Ryabov, A.D.; Schramm, K.; Collins, T.J., FeIII–TAML-catalyzed green oxidative degradation of the azo dye Orange II by H_2O_2 and organic peroxides:

products, toxicity, kinetics, and mechanisms, Green Chem. 9 (2007) 49–57.

Collins, T.J.; TAML oxidant activators: a new approach to the activation of hydrogen peroxide for environmentally significant problems, Accounts Chem. Res. 35 (2002) 782–790.

Clesceri, L.S.; Greenberg, A.E.; Trusel, R.R.; Franson, M.A., Standard methods for the examination of water and wastewater, 17th edition, American public health association and american water works association (1989), Washington, USA.

Duesterberg, C.K.; Mylon, S.E.; Waite, T.D., pH effects on Iron-catalyzed oxidation using Fenton's reagent, Environ. Sci. Technol. 42 (2008) 8522–8527.

Engelmann, M.D.; Bobier, R.T.; Hiatt, T.; Cheng, I.F., Variability of the Fenton reaction characteristics of the EDTA, DTPA, and citrate complexes of iron, BioMetals 16 (2003) 519–527.

Esplugas, S.; Giménez, J.; Contreras, S.; Pascual, E.; Rodríguez, M., Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

Fortuny, A.; Bengoa, C.; Font, J.; Castells, F.; Fabregat, A., Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, Catal. Today 53 (1999) 107–114.

Francis, K.C.; Cummins, D.; Oakes, J., Kinetic and structural investigations of [FeIII(edta)] - [edta = Ethylenediaminetetra-acetate(4-)] catalysed decomposition of hydrogen peroxide, J. Chem. Soc. Dalton Trans. (1985) 493–501.

Gupta, S.S.; Stadler, M.C.; Noser, A.; Ghosh, A.; Steinhoff, B.; Lenoir, D.; Horwitz, C.P.; Schramm, K.W.; Collins, T.J., Rapid total destruction of chlorophenols by activated hydrogen peroxide, Science 296 (2002) 326–328.

Haber, F.; Weiss, J., The catalytic decomposition of hydrogen peroxide by iron salts, Proc. R. Soc. London, Ser. A. 147 (1934) 332–351.

Jones, C.W.; Applications of hydrogen peroxide and derivates, Roy. Soc. Chem. London, (1999) pp. 264.

Kunz, A.; Peralta-Zamora, P.; Durán, N., Hydrogen peroxide assisted photochemical degradation of ethylenediaminetetraacetic acid, Adv. Environ. Res. 7 (2002) 197–202.

Li, L.; Abea, Y.; Kanagawa, K.; Shoji, T.; Mashino, T.; Mochizuki, M.; Tanaka, M.; Miyata, N., Iron-chelating agents never suppress Fenton reaction but participate in quenching spin-trapped radicals, Anal. Chem. Acta 599 (2007) 315–319.

Lin, S.H.; Chen, M.L., Treatment of textile wastewater by chemical methods for reuse, Water Res., 31 (1997), 868–876.

Matatov-Meytal, Y.I.; M. Sheintuch, Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309–326.

Neyens, E.; Baeyens, J., A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. B98 (2003) 33–50.

Nowack, B.; Sigg, L., Dissolution of Fe(III)(hydr)oxides by metal-EDTA complexes. Geochim. Cosmochim. Acta 61 (1997) 951–963.

Oakes, J.; Smith, E.G., Nuclear magnetic resonance studies of transition-metal complexes of Ethylenediamine-NNN'N'-tetramethylphosphonate in aqueous solution, J. Chem. Soc. Dalton Trans. (1983) 601–605.

Pera-Titus, M.; García-Molina, V; Baños, M.A.; Giménez, J.; Esplugas, S., Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

Pierce, E.M.; Wellman, D.M.; Lodge, A.M.; Rodriguez, E.A., Experimental determination of the dissolution kinetics of zero-valent iron in the presence of organic complexants. Environ. Chem. 4 (2007) 260–270.

Pignatello, J.J.; Oliveros, E.E.; Mackay, A., Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Critical Rev. Environ. Sci. Technol. 36 (2006) 1–84.

Rahhal, S.; Richter, H.W., Reduction of hydrogen peroxide by the ferrous iron chelate of diethylenetriamine-N,N,N',N",N"-pentaacetate, J. Am. Chem. Soc. 110 (1988) 3126–3133.

Rämö, J.; Sillanpää, M., Degradation of EDTA by hydrogen peroxide in alkaline conditions, J. Clean. Prod. 9 (2001) 191–195.

Rush, J.D.; Maskos, Z.; Koppenol, W.H., Distiniction between hydroxyl radical and ferryl species, Methods Enzymol. 186 (1990) 148–156.

Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, S.; García-Ochoa, F., Route of the catalytic oxidation of phenol in aqueous phase, Appl. Catal. B: Environ. 39 (2002), 97–113.

Sharma, V.K.; Millero, F.J.; Homonnay, Z., The kinetics of the complex formation between iron(III)–ethylenediaminetetraacetate and hydrogen peroxide in aqueous solution, Inorganica Chim. Acta 357 (2004) 3583–3587.

Sillanpää, M.; Pirkanniemi, K.; Sorokin, A., Oxidation of EDTA with H_2O_2 catalysed by metallophthalocyanines, Environ. Technol. 30 (2009) 1593–1600.

Sun, Y.; Pignatello, J.J., Chemical treatment of pesticide wastes: evaluation of Fe(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH, J. Agric. Food Chem. 40 (1992) 322–327.

Szpyrkowicz, L.; Juzzolino, C.; Kaul, S.N., A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, Water Res. 35 (2001) 2129–2136.

Tachiev, G.; Roth, J.A.; Bowers, A.R., Kinetics of hydrogen peroxide decomposition with complexed and “free” iron catalysts, Int. J. Chem. Kinet. 32 (2000) 24–35.

Walling, C.; Kurz, M.; Schugar, H.J., The Iron(III)-Ethylenediamine tetraacetic Acid-Peroxide system, Inorg. Chem. 9 (1970) 931–937.

Walling, C., Fenton´s reagent revisited, Accounts Chem. Res. 8 (1975) 125–131.

Wingate, K.G.; Stuthridge, T.R.; Wright, L.J.; Horwitz, C.P.; Collins, T.J., Application of TAML catalysts to remove colour from pulp and paper mill effluents, Water Sci. Technol. 49 (2004) 255–60.

Wink, D.A.; Nims, R.W.; Desrosiers, M.F.; Ford, P.C.; Keefer, L.K., A kinetic investigation of intermediates formed during the Fenton reagent mediated degradation of N-Nitrosodimethylamine: Evidence for an oxidative pathway not involving hydroxyl radical, Chem. Res. Toxicol. 4 (1991) 510–512.

CHAPTER 4

Catalytic wet peroxide oxidation of phenol using nanoscale zero-valent iron supported on activated carbon[2]

The main objective of the work is to prepare catalysts based on nanoscale zero-valent iron supported on activated carbon (nZVI/AC) and to test their activity for catalytic wet peroxide oxidation (CWPO) of phenol. The catalysts were characterized by XRD, SEM, ICP and N_2 adsorption-desorption and their performance evaluated in terms of phenol and TOC removal. The effect of the initial phenol concentration and initial pH on the oxidation process was investigated. Possible leaching of iron from the catalyst into the aqueous solution was also examined. The experimental results indicate that the catalytic activity towards phenol degradation was found to be enhanced by nano scale zero-valent iron supported on activated carbon catalysts (nZVI/AC) compared to that of Fe/AC. In the range 150-1000 mg/L, phenol conversion above 90% can be reached using these catalysts after only 15 min of reaction and using the stoichiometric hydrogen peroxide for complete mineralization. The leaching observed is less than 4% of the total initial iron in the catalyst even after 120 min of reaction. It was also observed that the stability or reutilization of the catalyst is fairly good.

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[2] S.A. Messele, C. Bengoa, F. Stüber, A. Fortuny, A. Fabregat, J. Font, Catalytic wet peroxide oxidation of phenol using nanoscale zero-valent iron supported on activated carbon. Under review in the Desalination and Water Treatment Journal.

4.1. Introduction

The treatment of refractory organic compounds such as phenol and its derivatives from industrial wastewater is of interest due to their biotoxic properties (Matatov-Meytal et al., 1998). Phenol is often taken as model compound for wastewater treatment examination, because it appears as starting or intermediate compound in many chemical, petrochemical and pharmaceutical process industries and also it is formed in the oxidation pathway of higher-molecular-weight aromatic hydrocarbons (Fortuny et al., 1999; Santos et al., 2002).

Various methods are widely studied for the removal of phenol such as biological treatment, extraction, and wet oxidation (Kujawski et al., 2004; Pera-Titus et al., 2004; Fang et al., 2006; Santos et al., 2006). However, advanced oxidation processes (AOPs) such as Fenton, photo-Fenton, ozone oxidation, and photo-catalytic oxidation are successfully used for wastewaters containing high concentration of more toxic pollutants (Joshi and Shambaugh, 1982; Pérez et al., 2002; Amat et al., 2005; Busca et al., 2008). AOPs generate hydroxyl radical, a strong oxidant, which can completely degrade the pollutants and non-selectively mineralize into harmless products. Among these, the interest in the use of Fenton system for the removal of phenolic compounds in water is increasing because this method avoids the use of costly reactors, it can be done at room temperature and atmospheric pressure, H_2O_2 decomposition leads to harmless products, and it is easy to manage (Jones, 1999; Esplugas et al., 2002; Azbar et al., 2004; Perathoner and Centi, 2005; Pignatello et al., 2006; Caudo et al., 2007). However, its application to the treatment of real wastewater has been limited mainly due to the narrow operational pH range, the disposal of iron-containing waste sludge, which needs subsequent separation steps, and most importantly the loss of reagent activity resulting in high operational expenses. On the premise of reducing the operation cost, an alternative solution is proposed, which is based on the use of a heterogeneous catalyst consisting of home-made nano zero-valent iron particles supported on activated carbon (nZVI/AC).

Activated carbon is being used since decades ago as an excellent adsorbent and supporting material due to its unique properties in mechanical strength and porous structure (Rodríguez-Reinoso, 1998; Ahumada et al., 2002). On the other hand, several studies have demonstrated that zero-valent iron (ZVI) has been able to effectively oxidize various organic and inorganic pollutants in the presence of oxygen (Joo et al., 2005; Katsoyiannis et al., 2008). Thus, a modified Fenton process, which utilizes ZVI, has been explored as a potential technique to degrade different pollutants in wastewater (Kallel et al., 2009). For example, the degradation of organic compounds using ultrasound combined with the ZVI/H_2O_2 system under acidic conditions was studied by Bremner (Bremner et al., 2006; Chakinala et al., 2009), but in the above cases the degradation was always examined using high excess of hydrogen peroxide. In this alternative, the oxidation of the metallic iron generates in situ ferrous iron giving rise to an effective Fenton-type reaction. The main advantage of this process is the faster recycling of ferric iron at the iron surface to give ferrous iron which is one of the Fenton reagents (Bremner et al., 2006). Furthermore, the use of zero-valent iron/granular activated carbon (Fe^0/GAC) in the presence of ultrasound was also proven to give good results in the degradation of dyes (Liu et al., 2007).

Taking into consideration the aforementioned disadvantages of classical Fenton system and the advantage of using ZVI as a catalyst and AC as a good adsorbent, a strategy is proposed to synthesize heterogeneous nZVI/AC catalysts and investigate their performance on the CWPO of phenol aqueous solutions. The effect of the initial phenol concentration and pH over the oxidation process has been investigated. The possible leaching of iron from the catalyst into the aqueous solution and its homogeneous contribution has also been examined. Finally, the catalyst stability (regeneration and reusability) after reaction was also addressed.

4.2. Experimental

4.2.1 Materials

All chemicals were used without further purification. Phenol was an analytical standard purchased from Panreac (99% purity). Hydrogen peroxide (H_2O_2 30%wt), iron nitrate nonahydrate (98% purity), sulphuric acid (98% purity), sodium hydroxide (98% purity) were purchased from Sigma-Aldrich. The activated carbon (particle size 1.5 mm) was purchased from Merck. Deionised water was used to prepare all the aqueous solutions.

4.2.2 Catalyst preparation

The Fe/AC catalysts were prepared by incipient wetness impregnation with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. Prior to use, the commercial activated carbon was ground and sieved with US standard sieve to obtain 25-50 mesh (0.3-0.7 mm) uniform particles and washed with deionised water in order to remove residuals or fines adsorbed on the surface. Finally, it was dried in an oven at 105 ºC for 15 h. This sample was hereafter labelled as AC. The amount of ferrous nitrate needed for 9% wt of iron in the final catalyst was dissolved in the minimum amount of deionised water and added drop wise on the support (AC). After impregnation, the slurry was then left for 2 h at room temperature, dried overnight at 105 ºC and these dried slurry was divided into two portions and submitted to heat treatment under two different conditions in order to have catalysts having different iron state. In the first one, the AC was heat treated under a nitrogen flow at 400 ºC for 4 h. After this step, the Fe is in the form of Fe_2O_3 (see section 4.3.1, XRD results) and the catalyst was labelled as Fe/AC and in the second route, it was heat treated under a nitrogen flow at 400 ºC for 1 h, and then reduced at 400 ºC under a hydrogen flow for 3 h (Pineau et al., 2006; Meshesha et al.,2009). In this case the Fe is in the ZVI form (see section 4.3.1, XRD results) and this catalyst was labeled as nZVI/AC.

4.2.3 Characterization techniques

Specific surface area and pore volume of the catalysts were determined by N_2 adsorption/desorption at 77 K, using a Micromeritics ASAP 2000 surface analyser. The samples were outgassed overnight at 523 K prior to the adsorption analysis. The Fe content of the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) after microwave-assisted digestion of samples. X-ray diffraction (XRD) analysis using a Siemens model of D5000 diffractometer with Cu Kα (λ = 1.406 A) radiation was employed to determine the crystal structure and crystallinity of the catalyst (AC composite). The surface morphology was investigated by scanning electron microscopy (SEM) using a Philips model XL 30 apparatus operated at an acceleration voltage of 20 kV.

4.2.4 Adsorption and catalytic activity tests

All adsorption/oxidation assays were carried out in a magnetically stirred jacketed batch reactor. The reactor was filled with 100 mL of phenol solution of initial concentration 150 mg/L. The reaction temperature was set to 30 ºC and maintained constant by circulating water from a thermostatic bath through the jacket. The pH of the solution was adjusted to pH 3.0 with sulphuric acid when required. Once the temperature reached 30 ºC, the theoretical stoichiometric amount of H_2O_2 based on complete phenol mineralization (750 mg/L, 0.25 mL) and 100 mg of catalyst were added simultaneously to start the reaction. Phenol adsorption assays were carried out in the same conditions, without H_2O_2 addition.

During the reaction, liquid samples of 1 mL were periodically withdrawn. Then each sample was filtered with a syringe nylon filter of 0.45 µm (Teknokroma, ref.TR-200101) and placed in a glass vial (Agilent) for immediate analysis. Some experiments were conducted three times to check the reproducibility of the results and the experimental error was within ±3%.

4.2.5 Analytical methods

The concentration of phenol was quantified by means of a High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and a C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were performed with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL of sample.

The Total Organic Carbon (TOC) was measured in a TC Multi Analyzer 2100 N/C equipment (Analytic Jena) with a non-diffractive IR detector. Fe leached from the catalyst to the reaction media was determined by using Atomic Absorption Spectroscopy (AAS) at 249 nm.

The main parameters used to compare the results in the discussion section are the removal of phenol (X_{PhOH}) and TOC (X_{TOC}) which are respectively defined as:

$$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \tag{4.1}$$

where $[PhOH]_0$ is the initial concentration and $[PhOH]_t$ is the concentration at time t, and

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \tag{4.2}$$

where TOC_0 is the initial concentration and TOC_t is the concentration at time t.

4.3. Results and discussion

4.3.1 Catalyst characterisation

Table 4.1 lists the properties, i.e., surface area (S_{BET}), mesoporous surface area (S_{meso}), pore volume (V_{micro}) and Fe content of the original AC, Fe/AC and nZVI/AC catalysts. Surface area of Fe/AC catalyst was reduced from 1055 to 962 m^2 g^{-1} and total pore volume was reduced from 0.640 to 0.538 cm^3 g^{-1} compared to the original AC. In the case of ZVI/AC, surface area was reduced from 1055 to 978 m^2 g^{-1} and total pore volume was reduced from 0.640 to 0.544 $cm^3\ g^{-1}$. Similar results were also reported by Li and co-workers concerning the effect of nZVI loadings on the pore volume and surface area of their resulting resin-based hybrid (Li et al., 2007). In general, slightly decrease in surface area and total pore volume for both catalysts was observed with respect to the original AC. This indicates that the pores were partially blocked by the active iron species, irrespective of being oxidised or reduced. From the ICP-OES analysis, slight variations (<10%) are noticed between the expected and the determined iron content of the sample, which means that most of the soluble iron was incorporated onto the support and validates the catalyst synthesis procedure.

Table 4.1 Properties of the support and the supported catalysts

Catalyst	**S_{BET} ($m^2\ g^{-1}$)**	**S_{meso} ($m^2\ g^{-1}$)**	**V_{micro} ($cm^3\ g^{-1}$)**	**Fe load (wt %)**
AC	1055	200	0.640	0.31
Fe/AC	962	212	0.538	8.17
nZVI/AC	978	198	0.544	8.20

Microimages of the synthesized Fe/AC, nZVI/AC and the original AC are shown in Figure 4.1. As it can be seen, the original AC is highly porous and smooth, whereas, the supported Fe particles in the pores of AC are needle shaped.

In turn, the supported ZVI particles in the pores of AC are clusters of aggregates of round-shaped particles and, their particle size being approximately 80-190 nm in diameter. Figure 4.1b (nZVI/AC) shows that most of the nZVI particles were loaded into the pores and cracks rather than onto the outer surface as observed elsewhere (Zhu et al., 2009). This interestingly helps to allow the repeated use of the catalyst without loss of the iron particles as commented later.

The XRD analysis of AC, Fe/AC and nZVI/AC is shown in Figure 4.2. The zero valence state and crystalline structure of nZVI were confirmed by X-ray diffraction analysis for the sample nZVI/AC. For sample Fe/AC, the iron was in the form of Fe^{II} or Fe^{III} oxide.

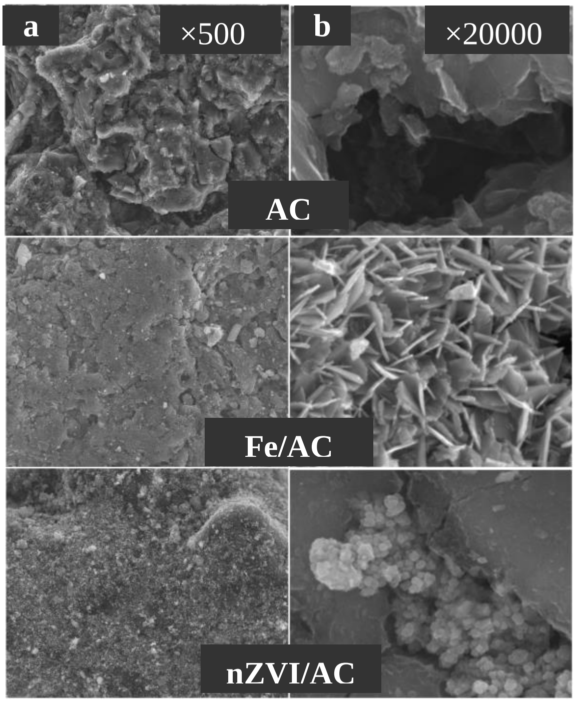

Figure 4.1 SEM images of the AC, Fe/AC and nZVI/AC (a) ×500 (b) ×20000

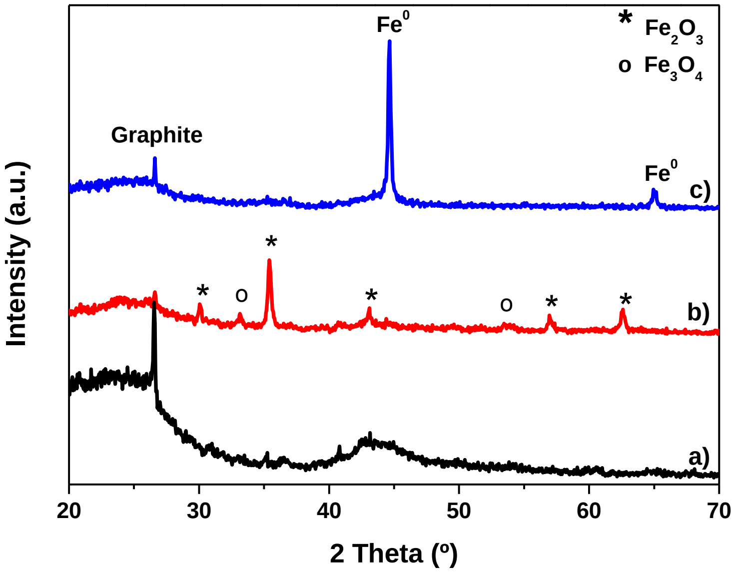

Figure 4.2 X-ray diffraction analysis of (a) AC, (b) Fe/AC and (c) nZVI/AC

4.3.2 Catalytic activity

4.3.2.1 Preliminary adsorption and oxidation tests

In first place, the potential catalytic performance of the iron containing carbon materials was demonstrated. Thus, tests using original activated carbon (AC), iron oxide loaded AC (Fe/AC) and the nZVI supported AC (nZVI/AC) were performed to check out their activity for phenol oxidation due to their iron state. The results are also contrasted against adsorption, i.e., without addition of hydrogen peroxide. The adsorption/oxidation tests were carried out using an initial concentration of phenol of 150 mg/L, 1 g/L of catalyst, 750 mg/L of H_2O_2, pH of 3.0, and 30 ºC.

Figure 4.3a illustrates the results for the phenol removal by adsorption (without H_2O_2) and oxidation using the different adsorbents/catalysts. The adsorption tests show that the original AC possesses a slightly higher adsorption capacity than that of the AC-supported samples, which is aligned with its somewhat greater surface area. In turn the adsorption capacity for both the supported samples is nearly the same, in accordance with their similar textural properties.

However, the results from phenol removal by peroxidation show that the AC-supported Fe or nZVI catalysts are capable of effectively decomposing phenol. It must be noted that AC alone does not shown relevant catalytic activity by itself in the tested conditions as the phenol disappearance profiles using virgin AC as a catalyst both in the absence and the presence of H_2O_2 are quite similar within 120 min, giving a final value of 65% and 73% of phenol removal, respectively. The slightly higher phenol disappearance in presence of H_2O_2, could be related to occurrence of natural iron content in small amounts (Table 4.1). Anyways, this indicates that oxidation of phenol is insignificant and phenol removal takes place mainly by adsorption in both cases. On the contrary, the AC containing supported Fe or nZVI enhances the initial rate, so after 60 min of reaction, the phenol removal is 83% for Fe/AC and already 99% for nZVI/AC.

It is worth that the nZVI/AC catalyst allows higher phenol removal (>90%) than that of Fe/AC (41%) after 15 min of reaction, it is because of the iron oxidation state as shown in the XRD spectra (Figure 4.2). The iron state in the Fe/AC catalyst is in the form of Fe_2O_3 and Fe_3O_4, whereas in the case of nZVI/AC catalysts, the iron is in the zero valent state, which has an advantage for Fenton chemistry. According to Segura et al (Segura et al., 2012; Segura et al., 2013), the oxidation of ZVI at acidic conditions generates in situ Fe^{2+}, Eq (4.3), which inturn promotes the generation of hydroxyl radicals (Eq. (4.4)) (Walling, 1975). The generated $^{\cdot}OH$ radicals are capable of oxidizing a wide range of organics in wastewater. The main advantage of this alternative (using ZVI as a source of Fenton reagent) is a faster recycling of ferric iron into ferrous species at the metallic iron surface through the reaction shown in Eq (4.5), so that they are more readily available throughout the reaction time.

$$ZVI + 2H^+ \longrightarrow Fe^{2+} + H_2 \qquad (4.3)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \qquad (4.4)$$

$$2Fe^{3+} + ZVI \longrightarrow 3Fe^{2+} \qquad (4.5)$$

Removal of TOC is presented in Figure 4.3b. The results illustrate that original AC, both in the absence and the presence of H_2O_2, provided the highest TOC removal after 120 min of reaction, above 64% compared to the AC-supported catalysts in respective of adsorption and oxidation tests.

Moreover, the TOC removal by adsorption for the AC-supported catalysts is relatively lower than that of the original AC but quite similar among them. Whereas, the TOC removal by oxidation for the first 15 min of reaction with the AC-supported catalysts is much better than that of the original AC but through time the TOC removal is not increasing as expected. This is related to the behaviour of AC as a very efficient adsorbent for phenol but not so good for some of its partial oxidation products during the oxidation of phenol. Thus, adsorbed phenol retains all its TOC content, so phenol removal by adsorption and TOC removal values are almost identical, within the experimental error, even coming from different measures. However, it must be noted that for AC in the absence of iron, the TOC is not actually destroyed but only adsorbed onto the AC.

On the contrary, when phenol is actually degraded by the hydrogen peroxide, the intermediate products are partially released back to the solution, apparently increasing the TOC content. In any case, the TOC removal by oxidation for nZVI/AC is better compared to Fe/AC catalysts, which leads to a conclusion that using nZVI/AC as catalyst enhances a deeper oxidation of phenol (Eftaxias wt al., 2006).

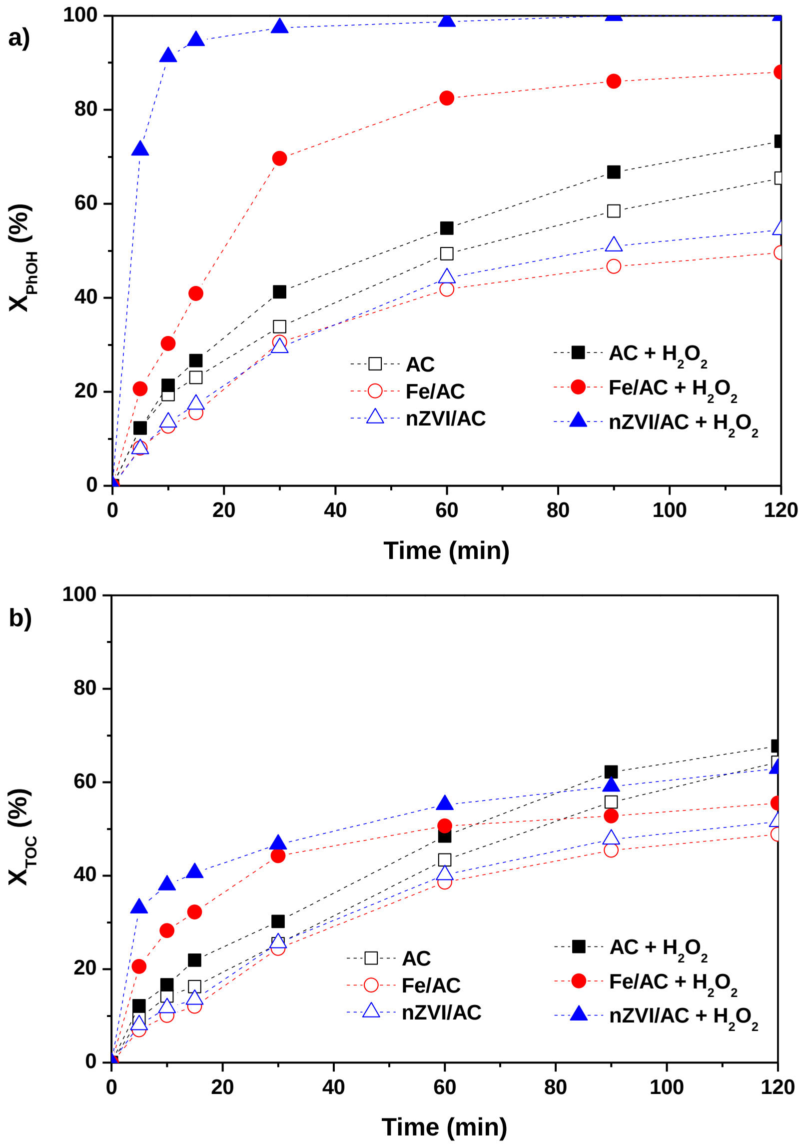

Figure 4.3 (a) Phenol and (b) TOC removal for different catalysts. (30 ºC, initial pH = 3.0, 150 mg/L of phenol, 1 g/L of catalyst, 750 mg/L of H_2O_2, 120 min). Open and full symbols represent results by adsorption and oxidation respectively

Some small contribution of homogeneous reaction may take place in the case of the AC-supported catalysts due to iron leaching. In order to know the total iron content in solution, samples were analysed by AAS at three reaction times (30, 60 and 120 min) for both adsorption and oxidation tests using Fe/AC and nZVI/AC catalysts. The obtained iron leached values for both catalysts are presented in Table 4.2.

Table 4.2 Leached iron after 30, 60 and 120 min of adsorption/oxidation tests for Fe/AC and ZVI/AC catalysis. (150 mg/L of phenol, 1 g/L of catalyst, 30 ºC, 750 mg/L of H_2O_2)

Samples	**Leached iron (%)**					
	In adsorption tests			**In oxidation tests**		
	30 min	**60 min**	**120 min**	**30 min**	**60 min**	**120 min**
Fe/AC	0.75	1.51	2.32	1.31	1.50	2.81
nZVI/AC	0.83	1.42	2.54	1.25	2.05	3.12

The results show that the iron leaching during phenol adsorption tests is quite similar for both Fe/AC and nZVI/AC catalysts, giving less than 1% after 30 min, lower than 1.5% after 60 min and below 2.5% after 120 min. Nevertheless, it is important to highlight that iron leaching from both catalysts during the phenol oxidation tests is slightly higher than that of adsorption tests; especially at longer time of reaction. This is because of the decrease of solution pH due to the intermediates formation, so more acidic pH favours iron leaching according to (Rey et al., 2009). For instance, iron leaching from the nZVI/AC catalyst after 120 min of reaction is slightly higher than that of Fe/AC, which is 3.12% and 2.80% respectively, but the iron leaching at shorter time (30 min) of reaction is quite similar for both catalysts. Therefore, the enhancement of the initial reaction rates of the nZVI/AC catalyst can not be related with the amount of iron leached. However, in terms of stability, in all the cases, the leaching of active phase (Fe) is insignificant as it is below 4%. Overall, the leaching is reasonable as only less than 4% of the total initial iron in the catalyst is lost, even after 120 min of reaction.

4.3.2.2 Effect of initial phenol concentration

The effect of the initial phenol concentration was investigated in the range of 150–1000 mg/L at pH 3.0 and 30 ºC with the addition of 100 mg of nZVI/AC and the stoichiometric ratio of H_2O_2. Figure 4.4a shows the phenol conversion evolution as a function of reaction time for the four initial phenol concentrations studied.

All the curves revealed a similar trend. As expected, the higher the phenol initial concentration, the greater the time required for total phenol conversion. Anyway, above 90% phenol removal was still obtained within 15 min reaction with an initial phenol concentration of 1000 mg/L. After 10 min, the phenol conversion obtained was 91%, 88%, 86% and 83%, respectively for 150, 250, 500 and 1000 mg/L.

As it can be seen in Figure 4.4b, the TOC conversion of the experiments for the four initial phenol concentrations were 55% for 150 mg/L, 51% for 250 mg/L, 37% for 500 mg/L and 35% for 1000 mg/L after 2 h of reaction. These values indicate that mineralization also correlate with the initial phenol concentration and deeper oxidation mainly took place for the lower phenol concentration.

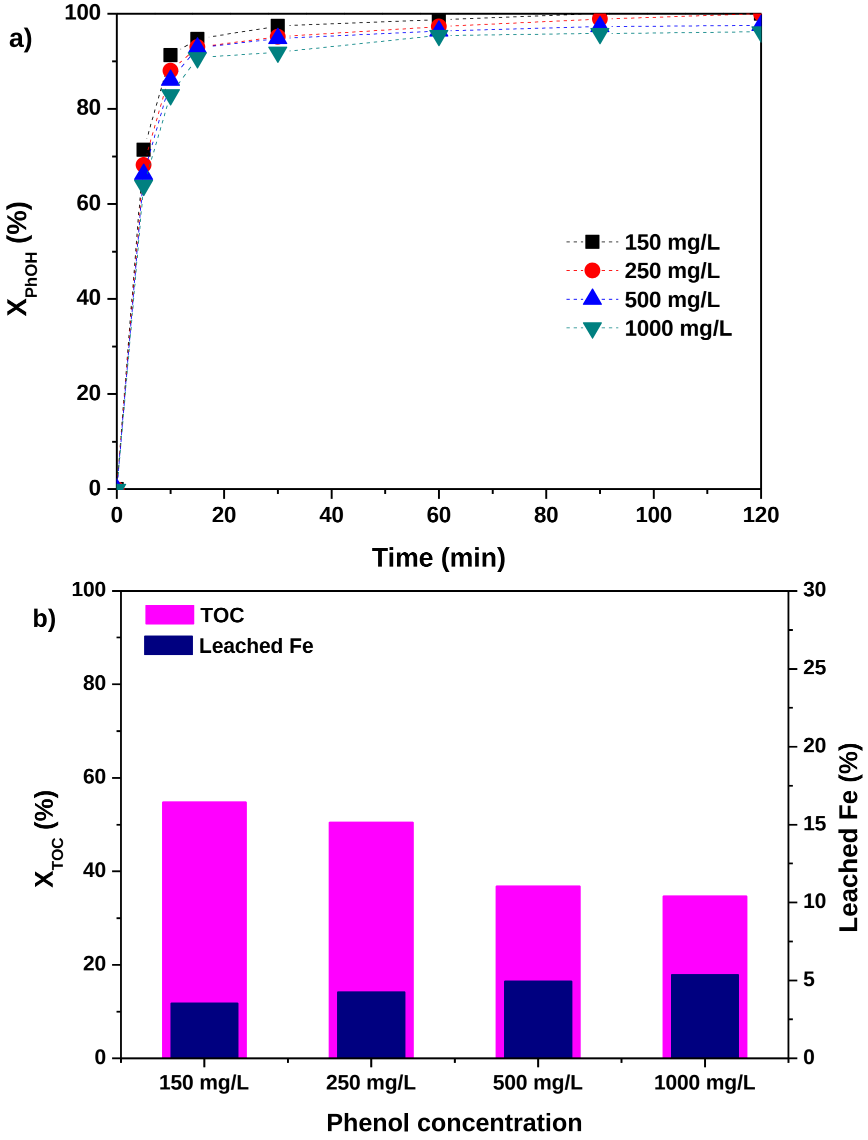

Figure 4.4 (a) Phenol removal versus time and (b) TOC removal and Leached Fe (%) after 120 min of reaction for different initial concentrations of phenol. (1 g/L of nZVI/AC, 30 ºC, pH 3.0, stoichiometric ratio of H_2O_2, and 120 min)

As in the previous cases, some iron leaching was observed during the reaction. Maximum of 5% iron leaching is observed for the highest concentration of phenol (1000 mg/L). For higher concentration of phenol the leaching is relatively high, this is probably related to the amount of peroxide used. i.e., the concentration of peroxide is dependent on the actual concentration of phenol as we used a stoichiometric ratio for the same amount of catalyst.

4.3.2.3 Effect of initial pH

It is well known that the optimum pH for homogeneous Fenton process is around 3.0 (Santos et al., 1999; Pignatello et al., 2006). At higher pH, the precipitation of the insoluble iron hydroxides takes place and the rate of of H_2O_2 decomposition decreased. This is the major limitation of the wet peroxide oxidation process because it needs previous acidification of the initial solution and later subsequent separation of the precipitated iron. Nowadays, the design of heterogeneous catalysts working in a wide range of pH is a big challenge. In order to investigate the influence of pH on the present study, the experiments were conducted at three pH values. First, H_2SO_4 was added to the phenol solution to adjust the initial initial pH value to 3.0. Second, NaOH was added to adjust the initial pH to 7.0. And finally, without any adjustment, naturally occuring pH of phenol (5.6) solution was left. Moreover, the effect of pH on the catalyst stability was also examined.

The increase of the pH evidently slows down the reaction rate. Figure 4.5 shows that the phenol removal for pH 3.0 is almost complete within 60 min of reaction, but for pH 5.6 and 7.0, the phenol removal drops up to 67% and 59%, respectively, after 120 min of reaction. On the other hand, the extent of Fe leaching decreases when the pH increases (Table 4.3).

Table 4.3 Effect of initial pH on Fe leaching from the catalyst after 30, 60 and 120 min of reaction (150 mg/L of phenol, 1 g/L of nZVI/AC, 30 ºC, 750 mg/L of H_2O_2)

Initial solution pH	Reaction time (min)	Leached Fe (%)
3.0	30	1.25
	60	2.05
	120	3.12
5.6	30	1.25
	60	1.46
	120	1.99
7.0	30	1.19
	60	1.23
	120	1.38

It is clear that the iron lost is higher for lower pH and this fact favors working at a higher pH values, in order to achieve long term stability. Nevertheless, the iron lost at shorter time of reaction is relatively comparable for all initial pH runs. For instance, after 30 min of reaction, the leached iron was 1.31%, 1.25% and 1.19% for the initial pH of 3.0, 5.6 and 7.0, respectively. Therefore, the leached iron can not be responsible for the higher activity of this catalyst, but the initial solution pH affects the initial reaction rates.

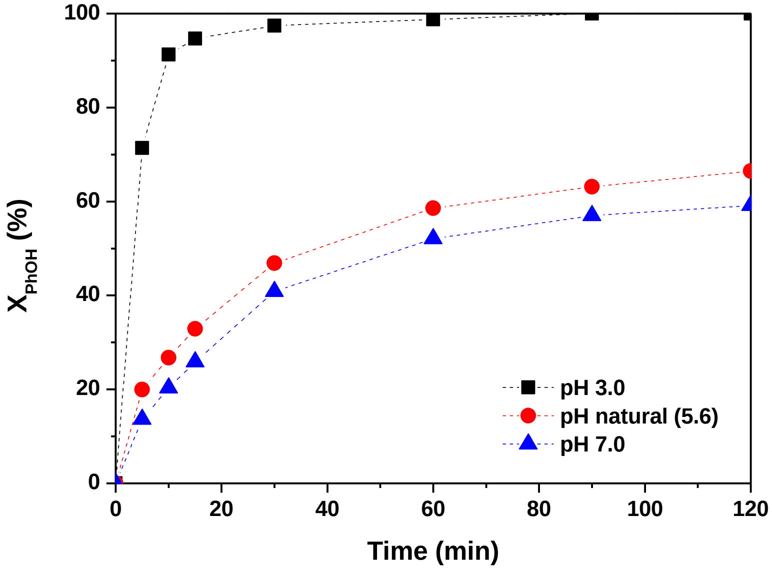

Figure 4.5 Phenol removal versus time for different initial solution pH of phenol. (150 mg/L of phenol, 1 g/L of nZVI/AC, 30 ºC, 750 mg/L of H_2O_2, 120 min)

4.3.3 Stability and recycling of nZVI/AC catalyst

It is important to evaluate the stability of the catalyst for heterogeneous catalytic system. For this purpose, consecutive runs were performed with the same catalyst. After each run, the used catalyst was filtered and washed with distilled deionised water. The sample was then dried at 105 ºC for 15 h, and then the CWPO of phenol was repeated with initial phenol concentration of 150 mg/L in the presence of the recycled catalyst and 750 mg/L of hydrogen peroxide at pH 3.0 and 30 ºC.

Figure 4.6 shows the phenol removal efficiency in three consecutive runs. Even though measurable activity decay is observed, phenol conversion decreases only from 100% to 93% in three runs after 120 min of reaction each. Considering shorter time, the catalyst is still able to yield about 90% phenol conversion at 60 min in the third run. Similar trend was also observed by Melero (Melero et al., 2007), after testing a Fe_2O_3/SBA-15 catalyst for the CWPO of phenolic aqueous solutions, they came up with the conclusion that the presence of residual organic compounds adsorbed on to the catalyst had a negative effect on its reusability.

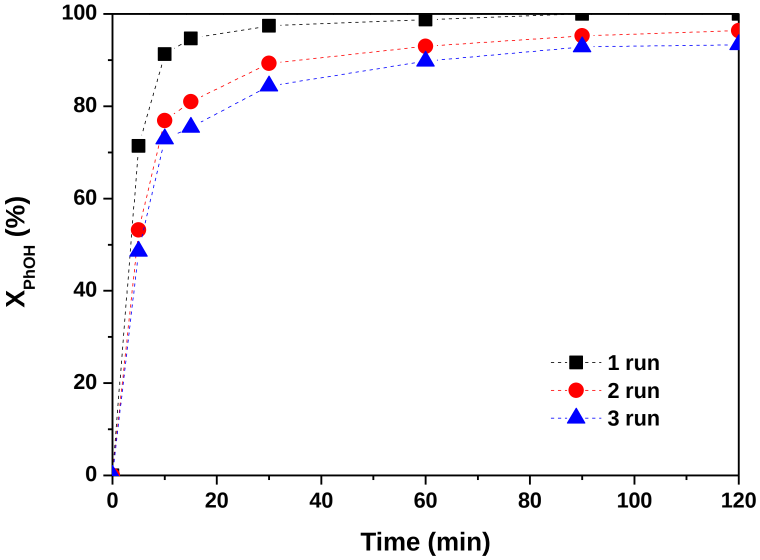

Figure 4.6 Phenol removal versus time for consecutive runs. (30 ºC, initial pH = 3.0, 150 mg/L of initial phenol concentration, 1 g/L of nZVI/AC, 750 mg/L of H_2O_2, 120 min)

Moreover, it must be considered that there was some loss of used catalyst during the filtration process for subsequent recycling. Table 4.4 summarizes the evolution of phenol removal, TOC removal and leached iron (%) upon reaction time with the recycled catalysts for the three consecutive runs.

Table 4.4 Catalytic behaviour of the catalyst after 30, 60 and 120 min of reaction for the three consecutive runs (30 ºC, initial pH 3.0, 150 mg/L of initial phenol concentration, 100 mg of nZVI/AC, 750 mg/L of H_2O_2)

Run	Time (min)	X_{PhOH} (%)	X_{TOC} (%)	Leached Fe (%)
1	30	97.4	46.7	1.25
	60	98.8	55.2	2.05
	120	100	62.9	3.12
2	30	89.3	37.2	0.50
	60	92.9	48.1	0.92
	120	96.4	56.6	1.74
3	30	84.4	32.4	0.83
	60	89.7	44.0	1.16
	120	93.3	53.3	1.77

As it can be observed, this catalyst showed a fairly good activity, allowing a TOC reduction of 53% after the third run. Furthermore, for the consecutive runs, the iron leaching is significantly reduced, around 1.8% of iron was found after 120 min of reaction after the third run, but the phenol conversion achieved remains remarkably unaltered.

In spite of this good stability, XRD characterization of the used catalysts was performed in order to know if ZVI survives or not. The XRD spectra in Figure 4.7 illustrate that the ZVI still appears after the three consecutive runs, though the intensity is a bit lower than that of the fresh catalyst. Moreover, for the used catalysts there is some Fe_2O_3 form of iron, which is already expected after the first run, because some of the iron has undergone oxidation at some extent during the reaction.

4.3.4 Homogeneous contribution

The active species leached from the catalyst may contribute to the phenol degradation through a homogeneous Fenton path. For this reason, an additional test was carried out to assess this possibility. A heterogeneous catalytic run was performed under typical conditions (30 ºC, 750 mg/L of H_2O_2, 100 mg of nZVI/AC and pH 3.0) for 30 and 120 min of reaction. The resultant solution was filtered to remove the catalyst and the clean liquid was collected, where 1.13 mg/L (1.25%) of leached iron specious was detected after 30 min of reaction and 2.80 mg/L (3.12%) of leached iron specious after 120 min of reaction. Then, phenol and hydrogen peroxide were further added to set again initial concentration of both in the filtered solution and a new reaction started to determine the homogeneous contribution.

The result (not shown) reveals that the phenol conversion for 1.13 mg/L of iron specious in homogeneous test was 41% after 120 min of reaction while for heterogeneous system the phenol conversion was completed just after 5 min of reaction. This clearly indicates that, the phenol conversion progress of this homogeneous test is much slower than that of the heterogeneous reaction. On the other hand, for the homogeneous test having 2.80 mg/L of iron specious in the filtered solution, phenol conversion was found to reach 71% after 120 min. This could be due to overestimation of the homogeneous contribution as we used the filtered solution after 120 min of the heterogeneous reaction. Therefore, according to these results, the overall activity of the catalyst is mainly due to heterogeneous phenomena and the contribution of the leached iron must be taken as secondary.

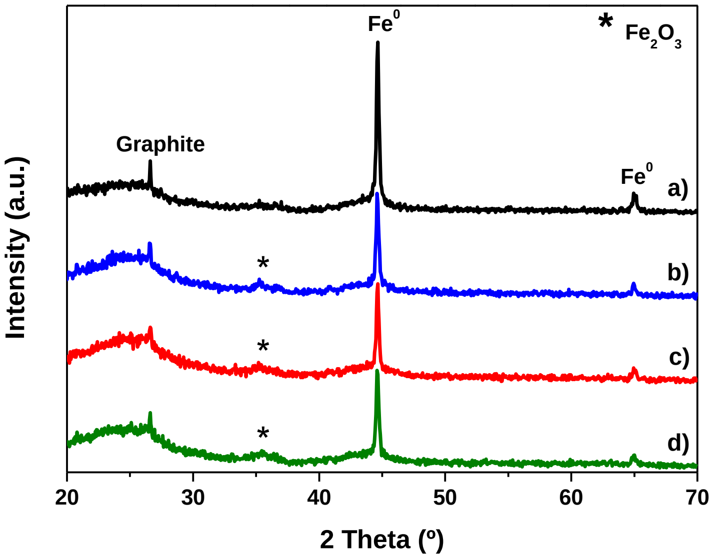

Figure 4.7 X-ray diffraction analysis of a) nZVI/AC (fresh catalyst), b) After 1st run c) After 2nd run and d) After 3rd run

4.4. Conclusions

In this study, nZVI/AC catalysts have been prepared and tested for CWPO of phenol in batch system. The SEM analyses indicated that nZVI were mostly found as clusters of aggregates of round-shaped particles and were loaded into the pores and cracks rather than onto outer surface. This interestingly allows the repeated use of the catalyst without noticeable loss of iron.

The heterogeneous catalyst performance in the adsorption and subsequent degradation of phenol has been examined. The catalytic activity towards phenol degradation was found to be enhanced by nano scale zero-valent iron supported on activated carbon catalysts. Phenol conversion above 90% can be reached using this catalyst after only 15 min of reaction using the stoichiometric hydrogen peroxide for phenol concentrations in the range 150-1000 mg/L.

The recycling and consecutive reutilization of catalyst gave final phenol removal nearly the same obtained with the fresh catalyst although at later time. In all the cases, the iron concentration leache into the solution was less than 5% and appears to be mostly independent of the reaction conditions. The leaching observed is not excessive as it means less than 5% of the total initial iron in the catalyst even after 120 min of reaction.

References

Ahumada, E.; Lizama, H.; Orellana, F.; Suárez, C.; Huidobro, A.; Sepúlveda-Escribano, A.; Rodríguez-Reinoso, F., Catalytic oxidation of Fe(II) by activated carbon in the presence of oxygen: Effect of the surface oxidation degree on the catalytic activity, Carbon 40 (2002) 2827–2834.

Amat, A.M.; Arques, A.; López, F.; Miranda, M.A., Solar photo-catalysis to remove paper mill wastewater pollutants, Sol. Energy, 79 (2005) 393–401.

Azbar, N.; Yonar, T.; Kestioglu, K., Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere 55 (2004) 35–43.

Bremner, D.H.; Burgess, A.E.; Houllemare, D.; Namkung, K.C., Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, Appl. Catal. B: Environ. 63 (2006) 15–19.

Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L., Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.

Caudo, S.; Centi, G.; Genovese, C.; Perathoner, S., Copper and iron-pillared clay catalysts for the WHPCO of model and real wastewater streams from olive oil milling production, Appl. Catal. B: Environ. 70 (2007) 437–446.

Chakinala, A.G.; Gogate, P.R.; Burgess, A.E.; Bremner, D.H., Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing, J. Chem. Eng. 152 (2009) 498–502.

Eftaxias, A.; Font, J.; Fortuny, A.; Fabregat, A.; Stüber, F., Catalytic wet air oxidation of phenol over active carbon catalyst: Global kinetic modelling using simulated annealing, Appl Catal B: Environ. 67 (2006) 12–23.

Esplugas, S.; Giménez, J.; Contreras, S.; Pascual, E.; Rodríguez, M., Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

Fang, H.H.P.; Liang, D.W.; Zhang, T.; Liu, Y., Anaerobic treatment of phenol in wastewater under thermophilic condition, Water Res. 40 (2006) 427–434.

Fortuny, A.; Bengoa, C.; Font, J.; Castells, F.; Fabregat, A., Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, Catal. Today 53 (1999) 107–114.

Jones, C.W.; Applications of hydrogen peroxide and derivates, Roy. Soc. Chem. : London, (1999) pp. 264.

Joo, S.H.; Feitz, A.J.; Sedlak, D.L.; Waite, D., Quantification of the oxidizing capacity of nanoparticulate zero-valent iron, Environ. Sci. Technol. 39 (2005) 1263–1268.

Joshi, M.G.; Shambaugh, R.L., The kinetics of ozone-phenol reaction in aqueous solutions, Water Res. 16 (1982) 933–938.

Kallel, M.; Belaid, C.; Mechichi, T.; Ksibi, M.; Elleuch, B., Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron, J. Chem. Eng. 150 (2009) 391–395.

Katsoyiannis, I.A.; Ruettimann, T.; Hug, S.J., pH dependence of Fenton reagent generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water, Environ. Sci. Technol. 42 (2008) 7424–7430.

Kujawski, W.; Warszawski, A.; Ratajczak, W.; Porebski, T.; Capała, W.; Ostrowska, I., Removal of phenol from wastewater by different separation techniques, Desalination 163 (2004) 287–296.

Li, A.; Tai, C.; Zhao, Z.; Wang, Y.; Zhang, Q.; Jiang, G.; Hu, J., Debromination of decabrominated diphenyl ether by resin-bound iron nanoparticles, Environ. Sci.Technol. 41 (2007) 6841–6846.

Liu, H.; Li, G.; Qu, J.; Liu, H., Degradation of azo dye Acid Orange 7 in water by Fe^0/granular activated carbon system in the presence of ultrasound, J. Hazard. Mater. 144 (2007) 180–186.

Matatov-Meytal, Y.I; Sheintuch, M., Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309–326.

Melero, J.A.; Calleja, G.; Martínez, F.; Molina, R.; Pariente, M.I., Nanocomposite Fe_2O_3/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions, J. Chem. Eng. 131 (2007) 245–256.

Meshesha, B.T.; Chimentào, R.J.; Medina, F.; Sueiras, J.E.; Cesteros, Y.; Salagre, P.; Figueras, F., Catalytic hydrodechlorination of 1,2,4-trichlorobenzene over Pd/Mg(Al)O catalysts, Appl. Catal. B: Environ. 87 (2009) 70–77.

Perathoner, S.; Centi, G., Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial streams, Top. Catal. 33 (2005) 207–224.

Pera-Titus, M.; García-Molina, V.; Baños, M.A.; Giménez, J.; Esplugas, S., Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

Pérez, M.; Torrades, F.; García-Hortal, J.A.; Domènech, X.; Peral, J., Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Appl. Catal. B: Environ. 36 (2002) 63–74.

Pignatello, J.J.; Oliveros, E.E.; Mackay, A., Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Critical Rev. Environ. Sci. Technol. 36 (2006) 1–84.

Pineau, A.; Kanari, N.; Gaballah, I., Kinetics of reduction of iron oxides by H_2 part I: Low temperature reduction of hematite, Thermochim. Acta, 447 (2006) 89–100.

Rey, A.; Faraldos, M.; Casas, J.A.; Zazo, J.A.; Bahamonde, A.; Rodríguez, J.J., Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, Appl. Catal. B: Environ. 86 (2009) 69–77.

Rodríguez-Reinoso, F., The role of carbon materials in heterogeneous catalysis, Carbon 36 (1998) 159–175.

Santos, A.; Barroso, E.; Garcia-Ochoa, F., Overall rate of aqueous-phase catalytic oxidation of phenol: pH and catalyst loading influences, Catal. Today 48 (1999) 109-117.

Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, S.; García-Ochoa, F., Route of the catalytic oxidation of phenol in aqueous phase, Appl. Catal. B: Environ. 39 (2002) 97–113.

Santos, A.; Yustos, P.; Gomis, S.; Ruiz, G.; Garcia-Ochoa, F., Reaction network and kinetic modeling of wet oxidation of phenol catalyzed by activated carbon, Chem. Eng. Sci. 61 (2006) 2457–2467.

Segura, Y.; Martínez, F.; Melero, J.A., Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron, Appl. Catal. B: Environ. 136–137 (2013) 64–69.

Segura, Y.; Martínez, F.; Melero, J.A.; Molina, R.; Chand, R.; Bremner, D.H., Enhancement of the advanced Fenton process (Fe^0/H_2O_2) by ultrasound for the mineralization of phenol, Appl. Catal. B: Environ. 113–114 (2012) 100–106.

Walling, C., Fenton´s reagent revisited, Accounts Chem. Res. 8 (1975) 125–131.

Zhu, H.; Jia, Y.; Wu, X., Removal of arsenic from water by supported nano zero-valent iron on activated carbon, J. Hazard. Mater. 172 (2009) 1591–1596.

CHAPTER 5

Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol [3]

Zero-valent iron supported catalysts were prepared through modifying an activated carbon (AC) support with different nitrogen containing precursors; (ethylenediamine, urea and melamine) and impregnating it with 3 wt% of iron. The supports were characterized by N_2 adsorption at -196 ºC, elemental analysis (EA), the pH at the point of zero charge (pH_{PZC}) and temperature programmed desorption (TPD). The iron catalysts were also characterized by temperature programmed reduction (TPR). Subsequently, the catalysts were tested in the adsorption and wet peroxidation of phenol. The results from the different characterization techniques demonstrate that the nitrogen-containing groups are successfully introduced into the carbon surface via all the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. Both surface chemistry and textural properties of carbons are influenced by the nitrogen source and the type of oxygen functionalities preexisting on the surface. The modified carbons supported iron catalysts revealed significantly enhanced phenol removal efficiency, reaching over 85% conversion after 3 h, and showed interesting catalytic stability.

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[3] S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol. Applied Catalysis B: Environmental 154–155 (2014) 329–338.

5.1 Introduction

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of wastewaters (Annadurai et al., 2000). Besides, due to the increasing complexity and toxicity of organic pollutants in industrial wastewaters and the more increasingly strict environmental regulations, the toxicity nature must be reduced. Phenol is among the most common water pollutants (Nayak and Singh, 2007; Paisio wt al., 2009) because it is presented in the effluent of numerous industrial processes such as oil refineries, petrochemical and pharmaceutical industries (Fortuny et al., 1999; Santos et al., 2002). This draws the attention of policymakers and scientists to take the necessary measures by studying alternative technologies, such as Advanced Oxidation Processes (AOPs).

AOPs are technologies based on the action of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds towards by-products and eventually inert end products (Mantzavinos and Psillakis, 2004; Comninellis et al., 2008). Among others, hydrogen peroxide, ozone or oxygen/air can be used as oxidizing agents, the processes being called wet peroxide oxidation (WPO), ozonation and wet air oxidation (WAO), respectively (Debellefontaine et al., 1999; Luck et al., 1999; García-Molina et al., 2005). Fenton process mainly operates under relatively mild operating conditions using hydrogen peroxide as oxidant and iron as a catalyst (Klavarioti et al., 2009).

Fenton process achieves good results so far. However, its application is mainly dependent on the narrow operational pH range, the loss of reagent activity and the need for a subsequent separation step to remove the homogeneous catalyst from the effluent, which significantly increases the cost of the operation (Pignatello et al., 2006). Therefore, taking into consideration the aforementioned inconveniences of Fenton system, a strategy is proposed to prepare a heterogeneous catalyst containing both the catalytic metal (iron) and N-functional groups on the surface of activated carbon (AC).

On one hand, it is well known that AC is widely used as a good adsorbent and supporting material due to its excellent properties in mechanical strength and porous structures (Rodríguez-Reinoso, 1998; Ahumada et al., 2002). On the other hand, the catalytic activity of AC is far from well understood. Besides the direct relationship with the physical properties (surface area, pore volume, etc.) of activated carbon (Eugeni et al., 2005), the surface chemistry can play an important role (Figueiredo et al., 1999;

Stüber et al., 2005; Quintanilla et al., 2007). According to the recent work of Dominguez et al. (Dominguez et al., 2013), the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition were explained using cyclic voltammetry, and the main results indicated that the most important factor in the catalytic activity was the content of metals, in particular iron, this was followed by the specific surface area and finally the content of surface oxygen groups.

In addition, the presence of a chelating agent in homogeneous Fenton has demonstrated to enhance the oxidation capacity (Klamerth et al., 2013), either by powering the oxidation potential or keeping the iron in solution at higher pH, although the addition of a new compound in solution is clearly an inconvenience (Yuan and VanBriesen, 2006). Although, some interest has been showed in using nitrogen-containing carbon materials as metal catalyst supports (Mabena et al., 2011), to the best of our knowledge, there are no data about their application in the catalytic wet peroxide oxidation (CWPO) process, but there are some recent studies on catalytic wet air oxidation (CWAO). Aminated activated carbon as a catalyst in the CWAO of cooking wastewater has been studied by Chen et al. (Chen et al., 2012). The COD removal in CWAO of organic compounds by nitrogen containing AC was higher than that of the untreated AC and suggested that nitrogen-containing functional groups contributed to the enhanced activities of ACs. A similar study was reported by Ayusheev et al. (Ayusheev et al., 2014), focusing on the effect of nitrogen content in N-doped carbon nanofibers (N-CNFs) on the catalytic activity of Ru/N-CNFs in the wet air oxidation of phenol. Ru-containing catalysts and nitrogen in N-CNFs was found to be responsible for both the increased activity and stability of the catalysts. Moreover, this study illustrates that the increase in catalytic activity is related with several factors: (1) introducing a heteroatom into carbon materials changes the acid-base properties of the support surface; (2) it makes possible to control the size of the supported metal particles; (3) using a support of higher conductivity leads to enhanced chemical reactivity for electron transfer process in a catalytic system.

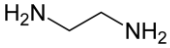
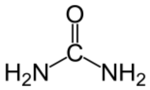
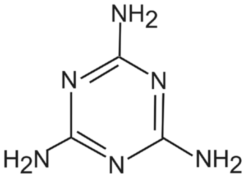
Therefore, the main objective of this work is to prepare surface modified activated carbon materials (for utilisation as supports/catalysts) using different N-containing groups, i.e. ethylenediamine (EDA), urea or melamine. Prior to introducing the N-functional groups on the AC surface, the activated carbon was oxidized by HNO_3 and/or subsequently activated by thionyl chloride treatment. Later, iron impregnated and then their performances were evaluated on phenol adsorption and wet peroxide oxidation.

5.2 Experimental

5.2.1 Materials

Activated carbon Norit ROX 0.8 was used as starting material for further treatments. Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30%wt), urea (98%), sodium hydroxide (≥97%) and iron nitrate nonahydrate (>98%) were purchased from Sigma-Aldrich. Ethylenediamine (>99%) was obtained from Merck. Thionyl chloride (>99%), melamine (≥99%) and toluene (>99%) were purchased from Fluka. The main physico-chemical properties of these N-containing compounds are presented in Table 5.1. All chemicals were used as received without further purification. Deionised water was used throughout the work.

Table 5.1 Chemical properties of the N-containing compounds used

N-containing compounds	Molecular formula	Molar mass (g mol^{-1})	Chemical structure	N content (wt. %)
Ethylenediamine	$C_2H_8N_2$	60.10		46.59
Urea	CH_4N_2O	60.06		46.62
Melamine	$C_3H_6N_6$	126.12		66.60

5.2.2 Modification of activated carbon supports and catalyst preparation

Prior to use, the Norit ROX 0.8 activated carbon was crushed and granules of 25 – 50 mesh size (0.3 – 0.7 mm) were separated and used as starting material (Sample AC0). Activated carbons were modified using a combination of surface modification protocols described below, in order to obtain supports having N-containing surface groups. Iron was then supported on these modified activated carbons by incipient wetness impregnation.

5.2.2.1 Oxidation with nitric acid in liquid phase

The starting activated carbon (sample AC0) was oxidized with HNO_3 using a 125 mL Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. A volume of 250 mL of 6 M HNO_3 was introduced into a 500 mL Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The oxidized activated carbon was extensively washed with distilled water to neutral pH and then dried in an oven at 110 ºC for 24 h (sample AC1) (Figueiredo et al., 1999).

5.2.2.2 Activation with thionyl chloride

Thionyl chloride was used as a linking agent on the surface of AC for the attachment of N-functional groups (Silva et al., 2002). About 12 g of the oxidized activated carbon (AC1) was subsequently activated with 40 mL of 5% solution of thionyl chloride in toluene for 5 h at 70 ºC. The carbon was then rinsed at least two times with toluene, and then purified by Soxhlet extraction with toluene for 2 h, and dried in an oven at 110 ºC for 24 h (sample AC2) (Lennox and Murray, 1977; Yantasse et al., 2004; Tamai et al., 2006).

5.2.2.3 Functionalization with ethylenediamine, urea and melamine

Samples AC1 and AC2 were the starting materials for functionalization with N-containing compounds. The functionalization of activated carbons with EDA, urea or melamine can be conducted directly (using sample AC1) or indirectly (using sample AC2). In the direct method, amine groups of these compounds condense with carboxyl groups on AC to generate surface amide groups. In the indirect method, they are anchored on the surface via a linkage agent thionyl chloride ($SOCl_2$). In this case, first the linking agent reacts with a carboxylic group of the surface to convert the surface carboxylic groups into acyl chloride functionalities (Silva et al., 2002); and in the second stage, the amine groups of EDA/urea/melamine condense with anchored chlorine atoms (Houshmand et al., 2012).

Ethylenediamine: 2 g of AC1 (or AC2) were refluxed with 100 mL solution of EDA in toluene (1 M) for 24 h. The amine grafted samples were washed in toluene under sonication for 10 min and then were purified in a Soxhlet extraction unit for 2 h to remove unattached or free EDA from activated carbon. The resulting activated carbons were dried in an oven at 110 ºC for 24 h (samples AC1_EDA and AC2_EDA).

Urea: 2 g of AC1 (or AC2) were added into 100 mL of an aqueous urea solution (1 M), and stirred at room temperature for 24 h. Then, the material was filtered and dried in the oven. The sample treated with urea was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10 ºC min^{-1} up to 450 ºC and held at this temperature for 50 min (samples AC1_Urea and AC2_Urea)

Melamine: 2 g of AC1 (or AC2) were mixed with a melamine suspension (1.3 g of melamine in 100 mL of 80% ethanol) and stirred at 70 ºC for 5 h. Then the mixture was boiled to evaporate the solvent and the slurry was dried at 110 ºC for 24 h. The sample impregnated with melamine was carbonized under N_2 flow (100 cm^3 min^{-1}) at 10 ºC min^{-1} up to 450 ºC and held at this temperature for 50 min (Bagreev et al., 2004; Sousa et al., 2013). After this treatment the samples are labeled as AC1_Melamine and AC2_Melamine, respectively.

5.2.2.4 Preparation of catalysts

The active metal was supported on the original (AC0) and in all the modified activated carbons by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under vacuum and ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110 ºC for 24 h and calcined under a nitrogen flow at 400 ºC for 1 h, then finally reduced at 400 ºC in hydrogen flow for 3 h (sample ZVI/support). The content of metal was maintained constant at 3 wt%. The reduction temperature for the iron catalysts was determined by temperature programmed reduction (TPR). The treatment methods for the activated carbon used in this work are summarized in Table 5.2.

Table 5.2 Abbreviations and description of original, modified and iron supported activated carbons

Abbreviation	**Description**
AC0	Untreated AC
AC1	HNO_3-treated AC0
AC2	$SOCl_2$-treated AC1
AC1_EDA	EDA-treated AC1
AC2_EDA	EDA-treated AC2
AC1_Urea	Urea- treated AC1
AC2_Urea	Urea- treated AC2
AC1_Melamine	Melamine- treated AC1
AC2_Melamine	Melamine- treated AC2
ZVI/ACx_y	Iron impregnated on sample ACx_y

x_y: represents the modification undergone on activated carbon

5.2.3 Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196 ºC, temperature programmed desorption (TPD), elemental analysis and determination of the pH at the point of zero charge (pH_{PZC}). The catalysts were also characterized by temperature programmed reduction (TPR).

5.2.3.1 Textural characterization

The textural characterization of all the materials was checked in order to evaluate if there had been significant textural changes after the modification of surface chemistry. This characterization was based on the N_2 adsorption isotherms, determined at -196 ºC with a Quanthachrome NOVA 4200e multi-station instrument. Prior to the measurements, the samples were outgassed at 120 ºC for 5 h under vacuum. The specific surface area of the mesopores (S_{meso}) and the micropore volume (V_{micro}) were calculated by the t-method. Moreover, the surface area (S_{BET}) of the samples was calculated by the B.E.T. method.

5.2.3.2 Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) analysis allows finding the most appropriate reduction temperature of the metal and to evaluate the effect of modified activated carbons on the reducibility. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The catalyst (0.15 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 600 ºC under a flow of 5% (v/v) H_2 in Ar at 30 cm^3 min^{-1}. The H_2 consumption was monitored by a thermal conductivity detector (TCD). The temperature range where reduction occurs could be indicated directly from the H_2 consumption peaks.

5.2.3.3 Surface chemistry characterization

The surface chemistry of the starting and modified activated carbons was characterized by temperature-programmed desorption (TPD) (Figueiredo et al., 1999). The TPD spectra of CO and CO_2 were obtained with a fully automated AMI-300 (Altamira instruments). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 1100 ºC under a constant flow rate of He at 25 cm^3 min^{-1} (STP). The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the carbon samples were monitored with a mass spectrometer (Dymaxion, Ametek). CO and CO_2 were calibrated at the end of each analysis.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH (Órfão et al., 2006).

Carbon, hydrogen, nitrogen and oxygen (by difference) contents were determined using a Carlo Erba EA 1108 Elemental Analyzer. Prior to the analysis, water adsorbed on the surface of the supports was removed by drying at 110 ºC in the oven overnight.

5.2.4 Adsorption and catalytic tests

Both adsorption and CWPO experiments were carried out in a magnetically stirred tank (batch reactor). The reactor was filled with 100 mL of a phenol aqueous solution (150 mg/L) and heated by immersion in a water bath at controlled temperature.

The solution pH was adjusted to a value of 3.0 using H_2SO_4 solution (1 M). When the desired temperature was reached (30 ºC), a calculated volume of H_2O_2 (0.25 mL) was added into the system after catalyst addition (100 mg), in order to reach a H_2O_2 concentration of 750 mg/L in the CWPO runs (the theoretical stoichiometric amount needed to completely mineralize phenol); at this moment the reaction was assumed to start. The CWPO oxidation runs were carried out both using the activated carbons (without iron) and iron supported carbon as catalysts, in order to evaluate the ability of the supports alone to decompose H_2O_2, and subsequently to promote phenol oxidation. This may give an idea to discriminate between a potential catalytic surface chemistry and the catalytic activity owing to the presence of iron.

In addition, pure adsorption runs were performed in order to assess the contribution of adsorption to the removal of phenol. The experiments were carried out in the same conditions, but without H_2O_2 addition.

Selected experiments were performed in triplicate and the relative error of the experimental results was below ±4%.

5.2.5 Analytical methods

Both in pure adsorption and in CWPO, liquid samples were periodically withdrawn from the reactor. Then, each sample was filtered with a syringe filter of 0.20 µm nylon (Teknokroma, ref._TR-200101) and placed in a glass vial (Agilent) for immediate analysis.

The determination of phenol concentration was performed by High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were carried out with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL.

Total Organic Carbon (TOC) was also determined at the end of the experiments in a TC Multi Analyzer 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector.

Fe leached to the reaction media was determined by using Atomic Absorption Spectroscopy (AAS) at 249 nm.

The main parameters used to compare the results in the discussion section are the removal of phenol (X_{PhOH}) and TOC abatement (X_{TOC}), which are respectively defined as:

$$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \tag{5.1}$$

where $[PhOH]_0$ is the initial phenol concentration and $[PhOH]_t$ is the concentration at time t, and

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \tag{5.2}$$

where TOC_0 is the initial TOC concentration and TOC_t is the concentration at time t.

5.3 Results and discussion

5.3.1 Characterization of activated carbons and catalysts

5.3.1.1 Textural properties

BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume (V_{micro}) of the original AC, modified AC and one iron supported catalyst are summarized in Table 5.3.

Table 5.3 Textural properties of samples

Sample	**S_{BET} (±10 m^2 g^{-1})**	**S_{meso} (±10 m^2 g^{-1})**	**V_{micro} (±0.01 cm^3 g^{-1})**
AC0	984	207	0.351
AC1	853	141	0.342
AC2	635	178	0.165
AC1_EDA	335	148	0.086
AC2_EDA	242	175	0.030
AC1_Urea	949	180	0.339
AC2_Urea	939	200	0.342
AC1_Melamine	194	111	0.038
AC2_Melamine	47	47	0.000
ZVI/AC0	975	216	0.348

The results revealed that the original AC (AC0) is highly microporous and has high BET surface area, 984 m^2 g^{-1}. In the case of acid-treated (AC1) and HNO_3 plus $SOCl_2$-treated (AC2) activated carbons, the BET surface area decreased following the treatments by 13% and 35%, respectively. The slight change in the surface area of AC1 can be explained by the abundant presence of oxygen-containing groups on the surface of the activated carbon, which are introduced by the HNO_3 treatment. In spite of having similar micropore volumes, AC0 and AC1 present different mesopore areas, suggesting that the mesostructure of activated carbon was partially destroyed after treatment with HNO_3. In the case of AC2, which is treated with HNO_3 and $SOCl_2$, the reduction in the surface area can be explained by the introduction of both oxygen and sulfur-containing groups. Such sulfur moieties (sulfones, sulfides, sulfoxides, and sulfur atoms) may lead to active sites occlusion inside the pores and on the surface of AC, as reported by Khayoon et al. (Khayoon and Hameed, 2011). Treatments with EDA and melamine lead to a drastic reduction of the surface area. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores. However, an appreciable increase of surface area and pore volume can be noticed only for urea treated samples (compared to AC1 and

AC2). In general, the textural properties of carbons are highly influenced by the nitrogen containing precursor; specially, for the AC2_Melamine sample, for which the micropore volume decreased up to nearly zero and also affects the mesostructure according to the S_{meso} value. On the other hand, the impregnation of iron did not substantially change the textural properties of the original carbon material due to the small load of iron (3 wt%) used, which is in agreement with the previous literature (Soares et al., 2009).

5.3.1.2 TPR

TPR profiles of iron catalyst on the different supports are shown in Figure 5.1. For comparison purpose, the TPR analyses of selected modified activated carbons were also performed and no additional peaks were observed. As it can be seen from Figure 5.1, the position, width and intensity of the peaks mainly depend on the nature of the support. The major reduction peak is at a temperature around 400 ºC for original (AC0) and oxidized AC (AC1). The second peak observed at temperature above 550 ºC in AC0 profile could be related to iron oxide which is strongly interacting with the support.

In general, the reduction peak for samples treated with N-containing compounds is shifted to the right irrespective of the starting material (AC1 or AC2). The reduction temperature depends on the degree of interaction between the active species and the support. For all samples treated with N-containing compounds using either AC1 or AC2 as a starting material, the iron reduction peaks shift to higher temperatures. Exceptions are the samples treated with urea, which present a reduction peak at lower temperature.

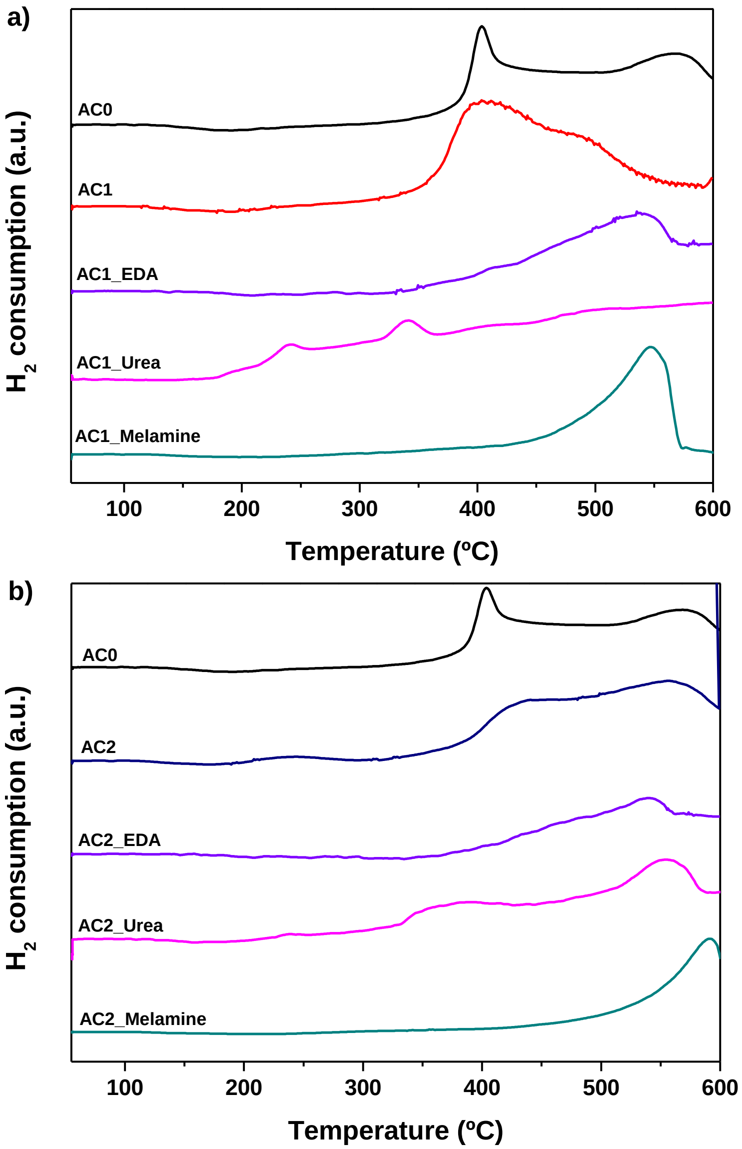


Figure 5.1 TPR profiles of supported iron catalysts using AC1 (a) and AC2 (b) as starting material

5.3.1.3 Surface chemistry characterization

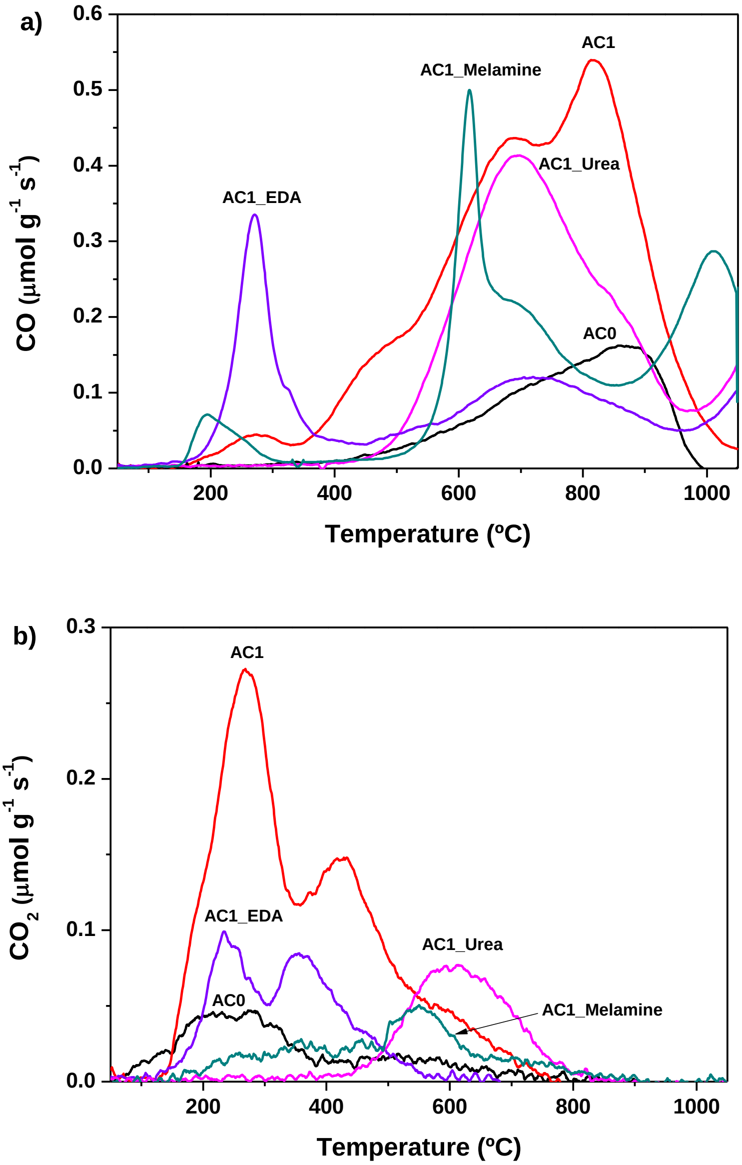
TPD and pH_{PZC}: TPD analyses were carried out to evaluate the surface chemistry of the different AC supports. The nature of the groups can be assessed by the decomposition temperature and the type of gas released. CO and CO_2 are released by thermal decomposition of oxygen containing groups on the surface of carbon materials at different temperatures

(Figueiredo et al., 1999). The TPD profiles of the original and modified activated carbons are depicted in Figure 5.2. From the TPD profiles, it is possible to identify and quantify the amounts of the oxygenated groups of each sample. CO_2 peaks result from carboxylic acids at low temperatures (150 – 450 ºC), or lactones at higher temperatures (600 – 800 ºC); carboxylic anhydrides originate both CO and CO_2 (400 – 650 ºC); groups such as phenols (600 – 800 ºC) and carbonyls/quinones (750 – 1000 ºC) originate CO peaks (Figueiredo et al., 2007).

It can be seen that the nitric acid treatment (AC1) increase the amount of oxygenated surface groups, which is evidenced by the increase of CO_2 (Figure 5.2a) and CO (Figure 5.2b) released. The samples treated with EDA originate CO peaks at lower temperatures (200-400 ºC) than the others.

As expected, AC1 has a low pH_{PZC} and the highest amount of CO and CO_2, due to the introduction of oxygen-containing surface groups having acidic properties, mainly carboxylic acids. After thionyl chloride treatment (sample AC2), the carboxyl groups were mostly converted into acid chloride groups, resulting a decrease of the amount of CO and $CO_{2,}$ but this material (AC2) still has acidic properties with the corresponding pH_{PZC} value similar to that of sample AC1. With the exception of AC2_EDA, all materials obtained after the treatment with N-containing precursors using sample AC1 or AC2 as starting materials have approximately neutral or slightly basic properties. This can be explained by the presence of nitrogen groups having basic properties.

In general, the TPD profile shows that it is important to have high density of oxygenated groups on the surface of carbon before functionalization with the N-containing compounds. The N-containing groups (EDA, urea and melamine) strongly interact with carboxylic acids, anhydrides and lactones (El-Sayed and Bandosz, 2005, Tamai ey al., 2006). Whereas, in the case of AC2, the N-functional groups were effectively introduced on the carbon surface via $SOCl_2$ linkage.


a)
CO (µmol g^{-1} s^{-1})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Temperature (ºC)
200
400
600
800
1000
AC1
AC1_Melamine
AC1_Urea
AC1_EDA
AC0
b)
CO$_2$ (µmol g^{-1} s^{-1})
0.0
0.1
0.2
0.3
Temperature (ºC)
200
400
600
800
1000
AC1
AC1_EDA
AC0
AC1_Urea
AC1_Melamine

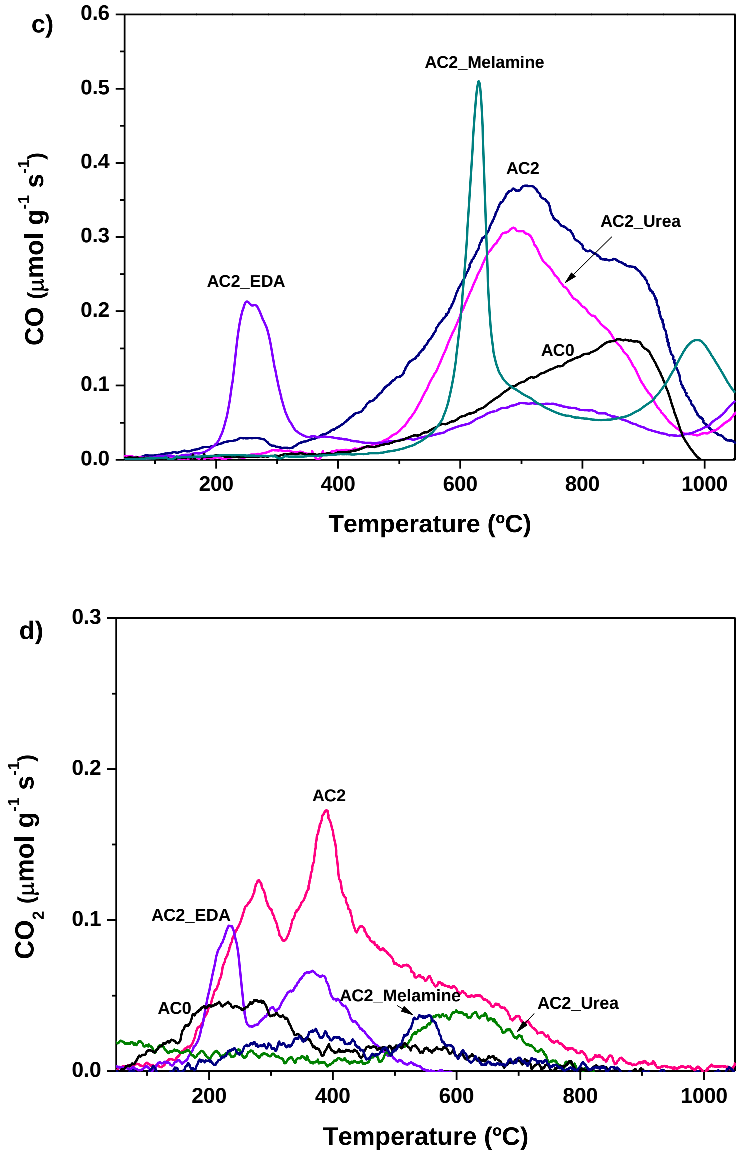


Figure 5.2 TPD spectra of the activated carbon supports (a) and (c) CO; (b) and (d) CO_2

The total amounts of CO and CO_2 released from the AC materials were calculated from the corresponding TPD spectra. This information as well as the point of zero charge of the samples with different surface chemistries are shown in Table 5.4.

Table 5.4 Surface chemistry data of activated carbon supports (total amounts of CO and CO_2 released, and pH_{PZC})

Sample	**CO (±20 μmol g^{-1})**	**CO_2 (±20 μmol g^{-1})**	**pH_{PZC} (±0.1)**
AC0	598	164	6.7
AC1	2311	754	2.5
AC2	1660	565	2.4
AC1_EDA	927	150	6.8
AC2_EDA	616	102	5.3
AC1_Urea	1481	193	7.6
AC2_Urea	1096	118	7.9
AC1_Melamine	1305	175	6.2
AC2_Melamine	739	102	6.7

***Elemental analysis**:* The carbon, hydrogen, nitrogen and oxygen contents obtained by elemental analysis are summarized in Table 5.5. Considering the treatment carried out, it was expected that AC2 and AC2-based samples may contain some sulphur, which is summed with the oxygen content as oxygen determined by difference.

Table 5.5 Elemental analysis of the original and modified AC

Sample	**C (wt%)**	**H (wt%)**	**N (wt%)**	**O^a(wt%)**
AC0	90.95	0.92	0.92	7.66
AC1	85.79	0.18	1.80	12.24
AC2	84.43	1.36	1.23	12.97
AC1_EDA	83.00	1.88	5.74	9.38
AC2_EDA	81.49	1.99	5.53	10.99
AC1_Urea	85.24	0.30	3.20	11.26
AC2_Urea	88.38	0.57	2.38	8.68
AC1_Melamine	81.69	0.74	15.95	1.62
AC2_Melamine	74.06	0.98	22.07	2.90

[a] Oxygen determined by difference.

The original AC contains a small amount (about 1%) of nitrogen. Significant amounts of nitrogen were introduced on the surface after treatment with N-containing compounds. The highest amount of nitrogen incorporated into the structure was obtained when melamine was the source of nitrogen, as its molecule contains up to six nitrogen atoms.

Thus, the differences in the amounts of nitrogen may be related to the content of nitrogen in the precursors (67% in melamine; 47% in urea and EDA) and the promoting effect of surface acidity, enhanced by oxidation/activation of $SOCl_2$ on the retention of N-containing organic bases (Bagreev et al., 2004; Seredych et al., 2008). On the other hand, the EDA treated samples contain a relatively high content of hydrogen compared to others; this is probably due to the higher content of hydrogen found in the compound. It is interesting to note that in the urea and EDA treated samples similar total contents of nitrogen are found regardless the pretreatment applied, either using oxidized (AC1) or activated with thionyl chloride (AC2). However, in the case of melamine treated samples, the nitrogen content is higher when the AC2 sample is the starting material in comparison to the inactivated (only oxidized) sample AC1.

5.3.2 Catalytic activity

Although it is difficult to compare the performance of catalysts having different textural properties and surface chemistries, we performed some tests using the activated carbons as adsorbents or catalysts and the iron supported on modified AC as catalysts for the removal of phenol in solution.

The phenol removal on the original and modified activated carbons was studied as a function of time under the following conditions: 100 mL of solution having 150 mg/L of phenol, adsorbent/catalyst amount = 1 g/L, initial pH of the solution = 3.0, T = 30 ºC, atmospheric pressure and stoichiometric amount of H_2O_2.

5.3.2.1 Adsorption experiments

Adsorption experiments were carried out to evaluate the effect of textural and surface properties of the original and modified activated carbons on phenol removal by adsorption. The results of phenol removal in adsorption runs performed with the original and modified activated carbons are compiled in Figure 5.3.

Even though the difference is not big compared to the original AC, it is clear that urea treated samples (AC1_Urea and AC2_Urea) improve the adsorption capacity of the original AC (AC0). These samples (AC0, AC1_Urea and AC2_Urea) present similar surface areas and pore volumes, their difference being mainly related with their surface chemistry. All the other materials showed lower adsorption capacities compared to the original AC. These adsorption results confirm that the textural properties of the carbon materials have a primary role in adsorption of phenol, irrespective of surface chemistry, but closely following the available surface area.

In the adsorption of aromatic compounds in liquid phase on activated carbons, there are mainly two types of interactions: (1) electrostatic and (2) dispersive (Moreno-Castilla, 2004). The first mechanism is involved when the adsorbate is dissociated under the experimental conditions. For example, if solution pH > pH_{PZC}, then the carbon surface is negatively charged, the opposite occurs when the solution pH < pH_{PZC} as described elsewhere (Radovic et al., 1997). In the case of the second mechanism, the existence of π-π dispersion interactions is commonly accepted (Haydar et al., 2003; Moreno-Castilla, 2004). Taking this in consideration, at pH of 3.0, phenol (pK_a=9.89) is found in solution predominantly in the molecular form and only the dispersive interactions are most probably involved in its adsorption on the carbon surface (Villacañas et al., 2006; Taran et al., 2010).

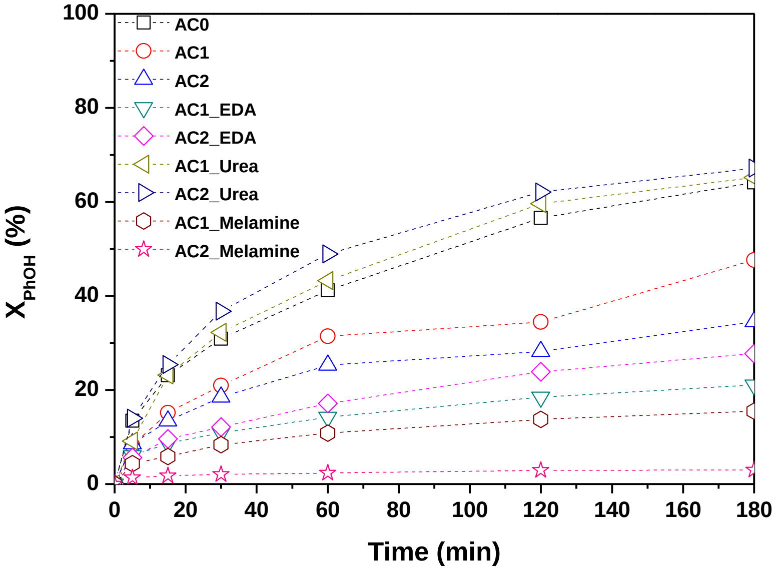


Figure 5.3 Phenol removal obtained in pure adsorption experiments (150 mg/L of phenol, pH 3.0, T = 30 ºC and adsorbent load = 1 g/L) with different carbon supports

Among the materials tested, the best performance was obtained with AC2_Urea, reaching 67% of phenol removal after 3 h. The BET surface area of this adsorbent is slightly lower and the pH_{PZC} is higher compared to the original AC. The EDA treated samples show moderate adsorption performance having moderate surface area and pH_{PZC}. However, the melamine treated samples show a poor adsorption performance due to the drastic decrease of surface area, though having a higher pH_{PZC} compared to AC1 and AC2 (pH_{PZC} of 2.5).

The presence of N-containing groups on the surface, increases the electronic density, and therefore the basicity of samples (see pH_{PZC} in Table 5.4), which generally favors adsorption of aromatic compounds. Recently, ammonia-modified activated carbon was prepared for the adsorption of 2,4-dichlorophenol (2,4-DCP), which enhances the adsorption capacity in comparison with the parent activated carbon (Shaarani and Hameed, 2011). This was explained due to the basic surface functional groups created by nitrogen-incorporation. Similar results also presented by Yang et al (Yang et al., 2014) for phenol adsorption using aminated activated carbon.

Moreover, the analysis of the results shows that there is a correlation between the phenol removal efficiency by adsorption and the S_{BET} of the tested activated carbons. The correlation is shown in Figure 5.4. The figure clearly shows that the phenol removal efficiency increases linearly with the S_{BET}, irrespective of the surface chemistry. This indicates that the surface area of activated carbons is the principal responsible for the phenol adsorption capacity. Fierro and co-workers (Fierro et al., 2008) also observed that the amount of adsorbed phenol in microporous activated carbons increases linearly with the increase in micropore volume.

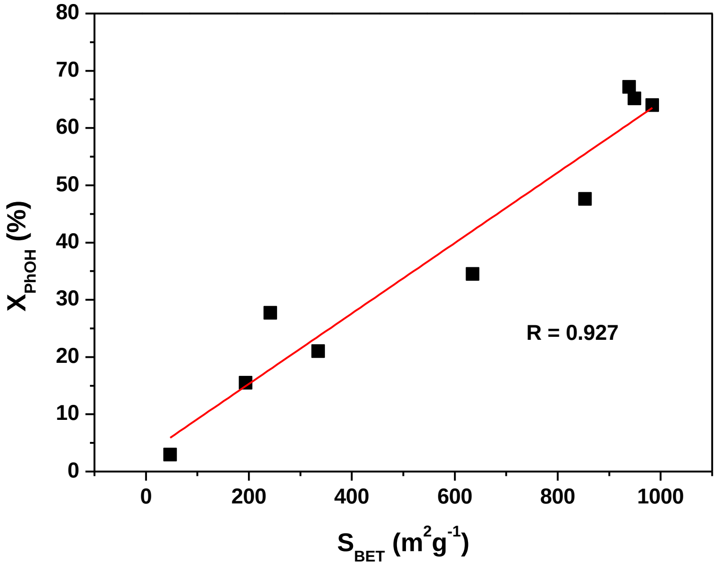


Figure 5.4 Correlation between specific surface area and phenol removal obtained in pure adsorption for original and treated activated carbons

As mentioned above, the textural and chemical properties of the tested samples are different. So, an additional study is needed to take conclusions about the effect of textural properties and surface functionalities. For this purpose, the apparent rate constants for the first-order (k_1) and second-order (k_2) adsorption models were determined for all samples tested. The constants of the two models are listed in Table 5.6. The ratio between k_1 or k_2 and S_{BET} is presented in the same table. Even though, both the first-order and the second-order model fit the experimental data quite well with R^2 values close to unity, the second-order model was suitable for the adsorption of lower molecular weight adsorbates on smaller adsorbent particles as reported by Wu et al. (Wu et al., 2009) and therefore the corresponding kinetic constants are used in the following discussion.

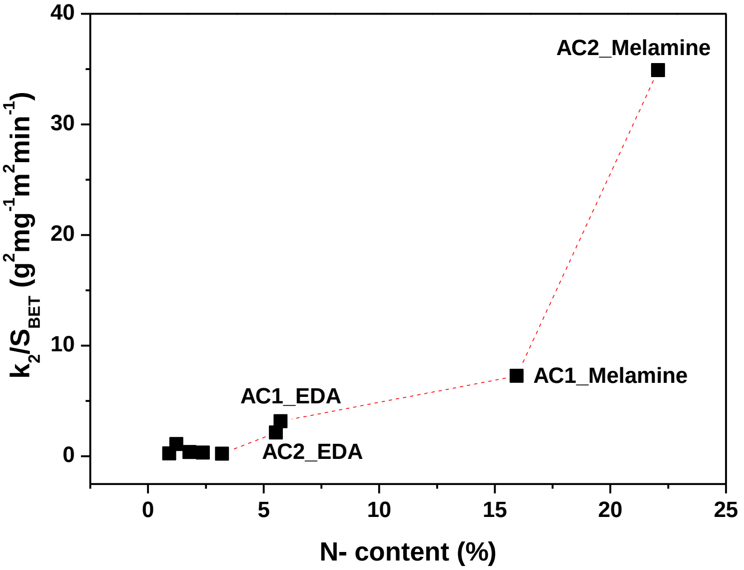


Figure 5.5 Plot of the normalized rate constants for phenol adsorption (k_2/S_{BET}) versus N-content for original and treated activated carbons

It is reported that phenol adsorption is dependent on both the surface area and the presence of surface groups (Fierro et al., 2008; stavropoulos et al., 2008). In order to evaluate the influence of the nitrogen content, the second-order apparent rate constants (k_2) are normalized by the specific surface area (S_{BET}). It can be observed in Figure 5.5 that high normalized adsorption rate constants correspond to samples with high amounts of N-containing surface groups (see Table 5.6).

Table 5.6 Kinetics parameters of the first-order and second-order adsorption models

Sample	**Pseudo-first-order**				**Pseudo-second-order**			
	qe (mg/L)	**k_1 (min^{-1})**	**R^2**	**10^3 k_1/S_{BET}**	**qe (mg/L)**	**10^3 k_2 ($g_{AC}mg^{-1}min^{-1}$)**	**R^2**	**10^6 k_2/S_{BET}**
AC0	80.87	0.017	0.988	0.017	104.10	0.268	0.981	0.272
AC1	54.52	0.011	0.891	0.013	73.52	0.336	0.951	0.394
AC2	37.35	0.014	0.915	0.022	52.08	0.706	0.983	1.111
AC1-EDA	25.27	0.016	0.978	0.047	33.89	1.060	0.982	3.164
AC2-EDA	36.29	0.015	0.987	0.062	47.39	0.522	0.972	2.157
AC1-Urea	84.76	0.020	0.992	0.021	108.69	0.228	0.995	0.240
AC2-Urea	83.62	0.021	0.995	0.022	107.52	0.309	0.996	0.329
AC1-Melamine	19.13	0.017	0.985	0.087	25.57	1.410	0.987	7.268
AC2-Melamine	3.39	0.028	0.965	0.596	4.65	1.640	0.995	34.890

5.3.2.2 CWPO experiments

***Modified activated carbons as catalysts**:* In order to evaluate the ability of the modified activated carbons to act as catalysts (without any supported metal) in the CWPO of phenol, runs were performed under the same conditions as the adsorption tests but now adding H_2O_2. The corresponding phenol removal curves are shown in Figure 5.6.

Phenol removal by CWPO in the presence of modified activated carbons as catalysts was similar or slightly higher than those obtained by adsorption. However, the results of phenol removal by adsorption (Figure 5.3) and CWPO (Figure 5.6) lead to the conclusion that these modified carbon materials are not particularly active for CWPO of phenol. For instance, the phenol removal at 60 min for AC1_Urea is 43% without H_2O_2 and 42% in the presence of H_2O_2, or 65% and 64%, respectively, at 180 min, which suggests that both cases are governed by adsorption. So, the removal of phenol is mainly due to pure adsorption. Similar conclusion was obtained in a previous work for some dyes (Santos et al., 2006). According to Dominguez et al (Dominguez et al., 2013), as the initial phenol concentration and the phenol/catalyst ratio used in the present work are relatively low, a large fraction of active sites on the carbon surface is available for hydrogen peroxide decomposition into hydroxyl radicals, which may be consumed by non-effective reactions. This probably explains the poor performance of activated carbon in CWPO compared to adsorption.

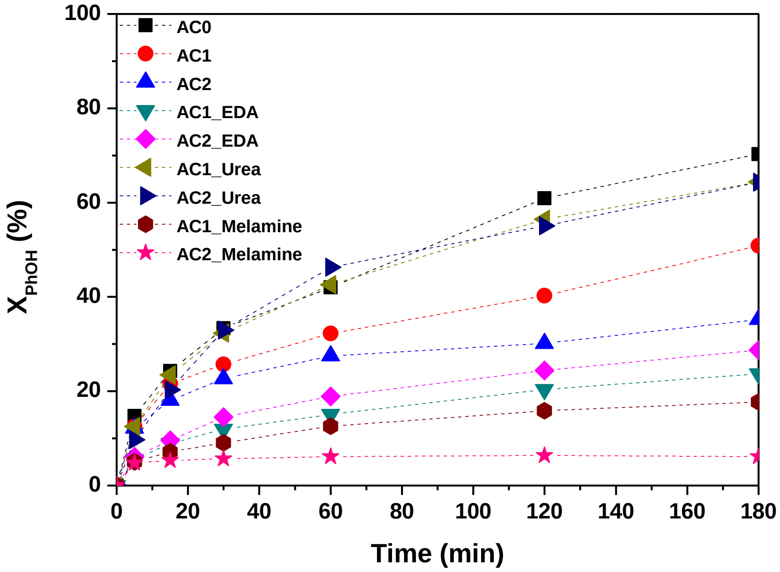


Figure 5.6 Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) with different activated carbons

Iron supported catalysts*:* In order to study the influence of surface chemical characteristics of the support on the activity of iron catalysts in phenol oxidation, a set of runs were performed in CWPO for different ZVI supported catalysts. Figure 5.7 shows the evolution of phenol removal in the presence of the iron catalyst supported on different supports. ZVI/AC2_Melamine and ZVI/AC2_EDA show a good and similar performance, reaching above 80% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e AC2_Melamine and AC2_EDA) shows low removal efficiency below 15 % after 60 min.

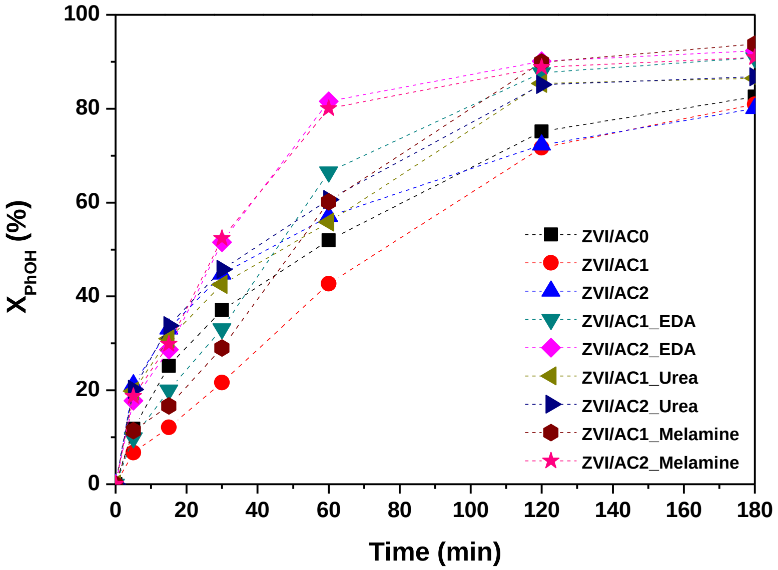


Figure 5.7 Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) with ZVI supported on different activated carbons

It must be strongly noted that the presence of ZVI on N-containing catalysts yields a better phenol removal, reaching values over 85% after 3 h. Here, ZVI acts as a heterogeneous catalyst for the degradation of phenol in aqueous solution by effectively decomposing hydrogen peroxide and generating hydroxyl radical, which reacts at high rate with phenol and its intermediates (Zhou et al., 2008). These results revealed that there is a direct and positive relation between the catalytic activity and the nitrogen content of the materials. Therefore, the activity of iron supported catalysts based on N-containing AC in CWPO of phenol is enhanced when compared to that of the untreated ones. It is thus observed that the presence of nitrogen groups on the surface of activated carbon, in addition to iron, clearly increases the phenol removal. This synergy can be probably assigned to the ability of retaining the iron ions close to the carbon surface due to the complexing properties of these N-containing groups.

Similar trends were observed for TOC removal at the end of adsorption and oxidation tests. Figure 5.8 shows that the EDA and melamine treated AC present lower TOC removal performance in the adsorption or oxidation tests when these materials were used as adsorbents or catalysts, respectively. However, the ZVI supported catalysts on the EDA and melamine treated supports also promote the TOC removal. The main reason for this can be explained by the synergetic effect of the presence of nitrogen group and iron on the surface of activated carbon, promoting oxidation instead of adsorption. In this case, the access of H_2O_2 to the iron on the carbon surface could be easier than for the other samples and accelerates the hydroxyl radical generation for deep oxidation of phenol, as observed in Figure 5.7. However, additional studies are still required to reveal the exact origin of these effects.

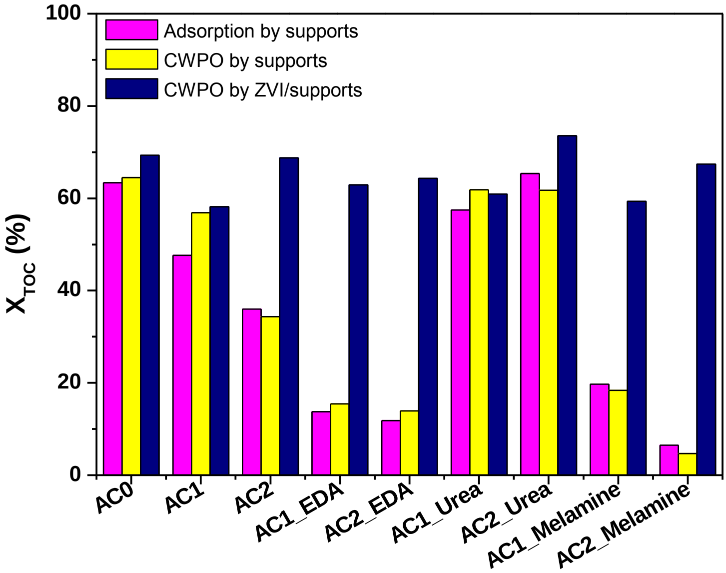


Figure 5.8 TOC removal after 180 min obtained in adsorption and CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and adsorbent/catalyst load = 1 g/L) with carbon samples and ZVI supported on activated carbons

Leaching tests were performed in order to evaluate the stability and contribution of homogeneous reaction for each catalyst after 120 and 180 min of reaction. Leaching of iron corresponds to values below 0.01% of the metal initially present in almost all catalysts; also limited values of 0.03 to 0.04% were measured in the case of AC1 and AC2 supported catalysts. This fact can be related with the pH_{PZC} of the support. In fact, AC1 and AC2 present the lowest pH_{PZC} and a relatively high iron leaching. In conclusion, the contribution of homogeneous system is quite negligible, as the amount of leached iron is quite low.

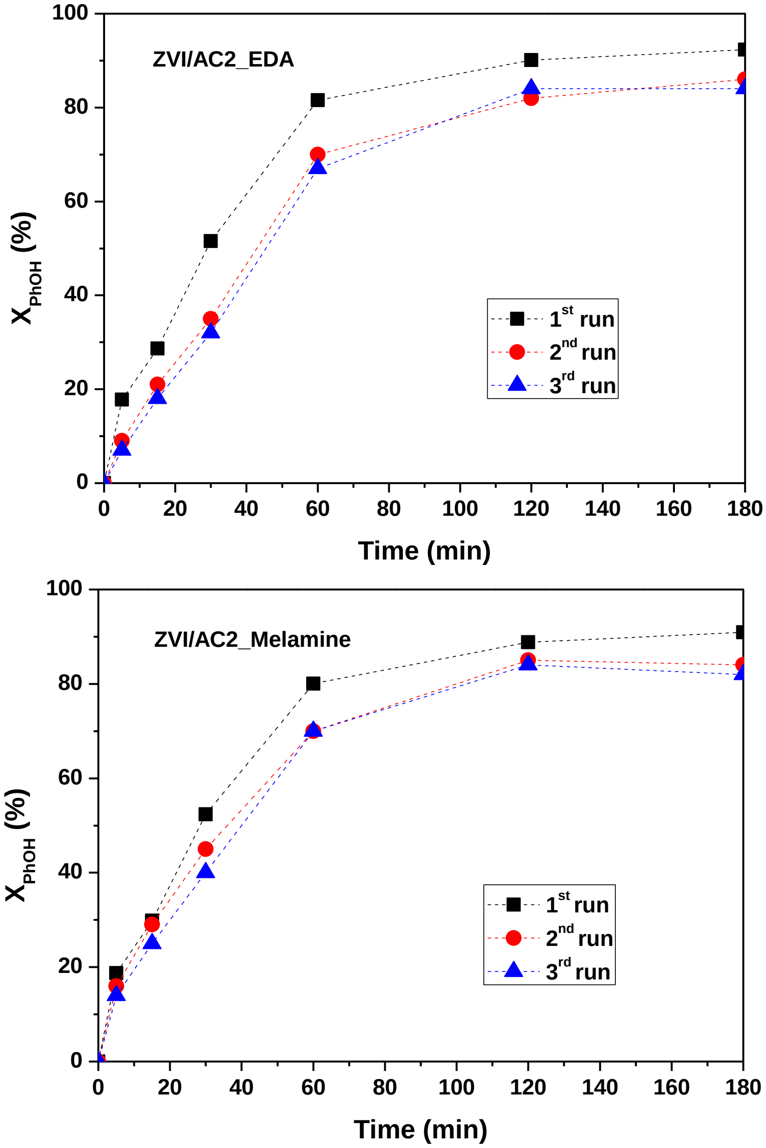


Figure 5.9 Phenol removal obtained by CWPO in sequential experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) using ZVI/AC_EDA and ZVI/AC2_Melamine catalysts

Since the stability of a catalyst is one important aspect in the general evaluation of its performance, the most efficient catalysts of this study (ZVI/AC2_Melamine and ZVI/AC2_EDA) were reused three times in consecutive CWPO reactions (Figure 5.9). A slight loss of catalyst activity is observed with both catalysts from the 1st to the 2nd run, but the activity being practically maintained from the 2nd to the 3rd run, and the actual removal of phenol is around 80%. The decrease in the removal of phenol observed from the first to the second run may be due to the lower adsorption capacity of the used catalyst and/or the slight loss of the catalyst during the recovery process. In fact, at the end of the experiment, a fraction of organic compounds will remain adsorbed onto the catalyst under the employed operating conditions. These compounds can be either phenol or intermediates formed during the oxidation reaction, as discussed elsewhere (Melero et al., 2007). In any case, both catalysts (ZVI/AC2_Melamine and ZVI/AC2_EDA) still present a good efficiency under consecutive runs.

5.4 Conclusions

Activated carbons with different N-containing precursors were modified, characterized and tested as adsorbents or catalysts for adsorption and peroxide oxidation of phenol. Besides, these modified carbons were also impregnated with iron and used as catalysts for CWPO.

Treatments with EDA and melamine lead to a drastic surface area reduction. This may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of N_2 molecules to the micropores.

In the urea and EDA treated samples similar total contents of nitrogen are found regardless of the pretreatment applied. However, in the case of melamine treated samples, the nitrogen content is significantly higher when the oxidized activated carbon treated with thionyl chloride is the starting material.

Phenol removal by CWPO in the presence of carbon materials was slightly higher than those obtained by adsorption. However, the results lead to the conclusion that these materials are not particularly active for the reaction, the removal of phenol being mainly due to adsorption.

The iron supported catalysts based on N-containing AC show the highest phenol removal efficiency, reaching values over 85% conversion after 3 h. This result revealed that there is a positive relation between the catalytic activity and the nitrogen content of the materials.

References

Ahumada, E.; Lizama, H.; Orellana, F.; Suárez, C.; Huidobro, A.; Sepúlveda-Escribano, A.; Rodríguez-Reinoso, F., Catalytic oxidation of Fe(II) by activated carbon in the presence of oxygen.: Effect of the surface oxidation degree on the catalytic activity, Carbon 40 (2002) 2827–2834.

Annadurai, G.; Babu, S.R.; Mahesh, K.P.O.; Murugesan, T., Adsorption and biodegradation of phenol by chitosan-immobilized Pseudomonas putida (NICM 2174), Bioprocess Eng. 2 (2000) 493–501.

Ayusheev, A.B.; Taran, O.P.; Seryak, I.A.; Podyacheva, O.Y.; Descorme, C.; Besson, M.; Kibis, L.S.; Boronin, A.I.; Romanenko, A.I.; Ismagilov, Z.R.; Parmona, V., Ruthenium nanoparticles supported on nitrogen-doped carbon nanofibers for the catalytic wet air oxidation of phenol, Appl. Catal. B: Environ. 146 (2014) 177–185.

Bagreev, A.; Menendez, J.A.; Dukhno, I.; Tarasenko, Y.; Bandosz, T.J., Bituminous coal-based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide, Carbon 42 (2004) 469–476.

Chen, H.; Yang, G.; Feng, Y.; Shi, C.; Xu, S.; Cao, W.; Zhang, X., Biodegradability enhancement of coking wastewater by catalytic wet air oxidation using aminated activated carbon as catalyst, J. Chem. Eng. 198–199 (2012) 45–51.

Comninellis, C.; Kapalka, A.; Malato, S.; Parsons, S.A.; Poulios, I.; Mantzavinos, D., Advanced oxidation processes for water treatment: advances and trends for R&D, J. Chem. Technol. Biotechnol. 83 (2008) 769–776.

Debellefontaine, H.; Crispel, S.; Reilhac, P.; Périé, F.; Foussard, J., Wet air oxidation (WAO) for the treatment of industrial wastewater and domestic sludge: design of bubble column reactors, Chem. Eng. Sci. 54 (1999) 4953–4959.

Domínguez, C.M.; Quintanilla, A.; Ocón, P.; Casas, J.A.; Rodriguez, J.J., The use of cyclic voltammetry to assess the activity of carbon materials for hydrogen peroxide decomposition, Carbon 60 (2013) 76–83.

Domínguez, C.M.; Ocón, P.; Quintanilla, A.; Casas, J.A.; Rodriguez, J.J., Highly efficient application of activated carbon as catalyst for wet peroxide oxidation, Appl. Catal. B: Environ. 140– 141 (2013) 663–670.

El-Sayed Y.; Bandosz, T.J., Role of surface oxygen groups in incorporation of nitrogen to activated carbons via ethylmethylamine adsorption, Langmuir 21 (2005) 1282–1289.

Fierro, V.; Torne-Fernandez, V.; Montane, D.; Celzard, A., Adsorption of phenol onto activated carbons having different textural and surface properties, Micropor Mesopor Mat. 111 (2008) 276–284.

Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.A.; Órfão, J.J.M., Characterization of Active Sites on Carbon Catalysts, Ind. Eng. Chem. Res. 46 (2007) 4110–4115.

Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.M.A.; Órfão, J.J.M., Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.

Fortuny, A.; Bengoa, C.; Font, J.; Castells, F.; Fabregat, A., Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, Catal. Today 53 (1999) 107–114.

García-Molina, V.; López-Arias, M.; Florczyk, M.; Chamarro, E.; Esplugas, S., Wet peroxide oxidation of chlorophenols, Water Res. 39 (2005) 795–802.

Haydar, S.; Ferro-Garcia, M.A.; Rivera-Utrilla, J.; Joly, J.P., A dsorption of p-nitrophenol on an activated carbon with different oxidations, Carbon 41 (2003), 387–395.

Houshmand, A.; Wan Daud, W.M.A.; Lee, M.; Shafeeyan, M.S., Carbon dioxide capture with amine-grafted activated carbon, Water Air Soil Pollut 223 (2012) 827–835.

Khayoon, M.S.; Hameed, B.H., Acetylation of glycerol to biofuel additives over sulfated activated carbon catalyst, Bioresour Technol. 102 (2011) 9229–9235.

Klamerth, N.; Malato, S.; Agüera, A.; Fernández-Alba, A., Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison, Water Res. 47 (2013) 833–840.

Klavarioti, M.; Mantzavinos, D.; Kassinos, D., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.

Lennox, J.C.; Murray, R.W., Chemically modified electrodes: VI. Binding and reversible electrochemistry of tetra-(aminophenyl) porphyrin on glassy carbon, J. Electroanal. Chem. 78 (1977) 395–401.

Luck, F.; Wet air oxidation: past, present and future, Catal. Today 53 (1999) 81–91.

Mabena, L.; Ray, S.; Mhlanga, S.; Coville, N., Nitrogen-doped carbon nanotubes as a metal catalyst support, Applied Nanoscience 1 (2011) 67–77.

Mantzavinos, D.; Psillakis, E., Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment, J. Chem. Technol. Biotechnol. 79 (2004) 431–454.

Melero, J.A.; Calleja, G.; Martínez, F.; Molina, R.; Pariente, M.I., Nanocomposite Fe_2O_3/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions, J. Chem. Eng. 131 (2007) 245–256.

Moreno- Castilla, C., Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon 42 (2004) 83–94.

Nayak, P.S.; Singh, B.K., Removal of phenol from aqueous solutions by sorption on low cost clay, Desalination 207 (2007) 71–79.

Órfão, J.J.M.; Silva, A.I.M.; Pereira, J.C.V.; Barata, S.A.; Fonseca, I.M.; Faria, P.C.C.; Pereira, M.F.R., Adsorption of a reactive dye on chemically modified activated carbons—Influence of pH, J. Colloid Interface Sci. 296 (2006) 480–489.

Paisio, C.E.; Agostini, E.; González, P.S.; Bertuzzi, M.L., Lethal and teratogenic effects of phenol on Bufo arenarum embryos, J. Hazard. Mater. 167 (2009) 64–68.

Pignatello, J.J.; Oliveros, E.E.; Mackay, A., Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Environ. Sci. Technol. 36 (2006) 1–84.

Quintanilla, A.; Casas, J.A.; Rodriguez, J.J.; Kreutzer, M.T.; Kapteijn, F.; Moulijn, J.A., Kinetics of the Wet Oxidation of Phenol over an Fe/Activated Carbon Catalyst, Int. J. Chem. Reactor Eng. 5 (2007) A62.

Radovic, L.R.; Silva, I.F.; Ume, J.I.; Menéndez, J.A.; Leon y Leon, C.A.; Scaroni, A.W., An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons, Carbon 35 (1997) 1339–1348.

Rodríguez-Reinoso, F., The role of carbon materials in heterogeneous catalysis, Carbon, 36 (1998) 159–175.

Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, S.; García-Ochoa, F., Route of the catalytic oxidation of phenol in aqueous phase, Appl. Catal. B: Environ. 39 (2002) 97–113.

Santos, V.P.; Pereira, M.F.R.; Faria P.C.C.; Órfão, J.J.M., Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons, J. Hazard. Mater. 162 (2009) 736–742.

Seredych, M.; Hulicova-Jurcakova, D.; Lu, G.Q.; Bandosz, T.J., Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance, Carbon 46 (2008) 1475–1488.

Shaarani, F.W.; Hameed, B., Ammonia-modified activated carbon for the adsorption of 2,4-dichlorophenol, J. Chem. Eng. 169 (2011) 180–185.

Silva, A.R.; Martins, M.; Freitas, M.M.A.; Valente, A.; Freire, C.; De Castro, B.; Figueiredo, J.L., Immobilization of amine-functionalized nickel(II) schiff base complexes onto activated carbon treated with thionyl chloride, Micropor Mesopor Mat. 55 (2002) 275–284.

Soares, O.S.G.P.; Órfão, J.J.M.; Pereira, M.F.R., Bimetallic catalysts supported on activated carbon for the nitrate reduction in water:

Optimization of catalysts composition., Appl. Catal. B: Environ. 91 (2009) 441–448.

Sousa, J.P.S.; Pereira, M.F.R.; Figueiredo, J.L., Modified activated carbon as catalyst for NO oxidation, Fuel Process Technol 106 (2013) 727–733.

Stavropoulos, G.G.; Samaras, P.; Sakellaropoulos,G.P., Effect of activated carbons modification on porosity, surface structure and phenol adsorption, J. Hazard. Mater. 151 (2008) 414–421.

Stüber, F.; Font, J.; Fortuny, A.; Bengoa, C.; Eftaxias, A.; Fabregat, A., Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater, Top Catal. 33 (2005) 3–50.

Suarez-Ojeda, M.E.; Stüber, F.; Fortuny, A.; Fabregat, A.; Carrera, J.; Font, J., Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst, Appl. Catal. B: Environ. 58 (2005) 105–114.

Tamai, H.; Shiraki, K.; Shiono, T.; Yasuda, H., Surface functionalization of mesoporous and microporous activated carbons by immobilization of diamine, J. Colloid Interface Sci. 295 (2006) 299–302.

Taran, O.; Polyanskaya, E.; Ogorodnikova, O.; Kuznetsov, V.; Parmon, V.; Besson, M.; Descorme, C., Influence of the morphology and the surface chemistry of carbons on their catalytic performances in the catalytic wet peroxide oxidation of organic contaminants, Appl. Catal., A, 387 (2010) 55–66.

Villacañas, F.; Pereira, M.F.R.; Órfão, J.J.M.; Figueiredo, J.L., Adsorption of simple aromatic compounds on activated carbons, J. Colloid Interface Sci. 293 (2006) 128–136.

Wu, F.C.; Tseng, R.L.; Huang, S.C.; Juang,R.S., Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review, J. Chem. Eng. 151 (2009) 1–9.

Yang, G.; Chen, H.; Qin, H.; Feng, Y., Amination of activated carbon for enhancing phenol adsorption: Effect of nitrogen-containing functional groups, Appl. Surf. Sci. 293 (2014) 299–305.

Yantasee, W.; Lin, Y.; Fryxell, G.E.; Alford, K.L.; Busche, B.J.; Johnson, C.D., Selective Removal of Copper(II) from Aqueous Solutions Using Fine-Grained Activated Carbon Functionalized with Amine, Ind. Eng. Chem. Res. 43 (2004) 2759–2764.

Yuan, Z.; VanBriesen, J.M., The formation of intermediates in EDTA and NTA biodegradation, Environ. Eng. Sci. 23 (2006) 533–544.

Zhou, T.; Li, Y.Z.; Ji, J.; Wong, F S.; Lu, X.H., Oxidation of 4-chlorophenol in a heterogeneous zero valent iron/H_2O_2 Fenton-like system: kinetic, pathway and effect factors, Sep. Purif. Technol., 62 (2008) 551–558.

CHAPTER 6

Effect of activated carbon surface chemistry on the activity of ZVI/AC catalysts for Fenton-like oxidation of phenol [4]

Activated carbons with different amounts of surface oxygenated groups were used as adsorbents or supports for zero-valent iron (ZVI) catalyst and tested in phenol adsorption and catalytic wet peroxide oxidation, respectively. The results revealed that the surface chemistry of the support plays an important role in phenol adsorption and in the catalytic performance of the respective iron-supported catalysts. ZVI is active when the support has only a limited amount of oxygenated groups on the surface. The presence of acidic oxygenated surface groups is not favorable for the catalytic activity of ZVI in phenol oxidation as well as for phenol adsorption. ZVI supported on activated carbon heat-treated at 900 ºC yields the best phenol removal, reaching over 85% after 3 h, under the conditions tested: 150 mg/L of initial phenol concentration, initial pH set at 3, 30 ºC, and the stoichiometric amount of hydrogen peroxide for achieving complete mineralization.

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[4] S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Effect of activated carbon surface chemistry on the activity of ZVI/AC catalysts for Fenton-like oxidation of phenol. Catalysis Today (In Press, DOI: 10.1016/j.cattod.2014.03.063).

6.1 Introduction

Degradation of refractory organic compounds such as phenol and derivatives from industrial wastewater is of interest due to their biotoxic properties (Matatov-Meytal et al., 1998; Nayak and Singh, 2007; Paisio et al., 2009). Oxidation techniques carried out at low temperature, as the Fenton process, are able to achieve good results (Pérez et al., 2002; Pignatello et al., 2006; Klavarioti et al., 2009). Nevertheless, its application to the treatment of waste water has been limited mainly due to the loss of reagent activity and the need of additional separation steps to remove the homogeneous catalyst (iron-containing waste sludge) from the effluent (Kang et al., 2002; Pignatello et al., 2006). To overcome these disadvantages, several studies have been performed to develop heterogeneous iron containing catalysts from different iron precursors and support materials, which will be able to generate the desired hydroxyl radicals in the presence of hydrogen peroxide (Guélou et al., 2003; Liou et al., 2005; Zazo et al., 2006; Rey et al., 2009).

Activated carbons have been used for many years as a good adsorbent and support, but also their use as catalysts on their own is growing (Fortuny et al., 1998; Rodríguez-Reinoso,1998; Rivera-Utrilla and Sánchez-Polo, 2002; Suarez-Ojeda et al., 2005; Figueiredo and Pereira, 2009). One of the advantages of activated carbon (AC) is the possibility of tailoring their physical and/or chemical properties in order to optimize their performance for specific applications (Pereira et al., 2004). Moreover, the surface chemistry can play an important role on the catalytic activity (Figueiredo et al., 1999; Stüber et al., 2005; Quintanilla et al., 2007).

In the present study, an alternative solution is proposed, which is based on the use of a heterogeneous catalyst consisting in a home-made zero-valent iron (ZVI) supported on surface modified activated carbon (MAC). The use of this zero-valent iron supported on surface modified activated carbon (ZVI/MAC) can easily overcomes the inconvenient subsequent catalyst separation. In addition, the oxidation of the metallic iron, generates *in situ* ferrous iron giving rise to an effective Fenton-type reaction, and also a fast recycling of ferric iron into ferrous iron at the metal surface, which leads to have continuous presence of iron metal for the generation of hydroxyl radicals (Bremner et al., 2006; Segura et al., 2012; Segura et al., 2013).

In this work, a commercial activated carbon (Norit ROX 0.8) was modified by chemical and thermal treatments in order to obtain supports with different surface chemistries, while maintaining the original textural properties as far as possible. The wet incipient impregnation was used for preparing iron catalysts supported on the different activated carbon supports. Then, the performance of the modified supports and catalysts on phenol adsorption and wet peroxide oxidation was evaluated in batch reactor and discussed.

6.2 Experimental

6.2.1 Materials

Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid, (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30%wt), sodium hydroxide (≥97%) and iron nitrate nonahydrate (>98%) were purchased from Sigma Aldrich. Activated carbon Norit ROX 0.8 was used as starting material for further treatments. All chemicals were used as received without further purification. Deionised water was used throughout the work.

6.2.1.1 Modification of activated carbon supports and catalyst preparation

Prior to use, the Norit ROX 0.8 activated carbon was crushed and the 25–50 mesh fractions (0.3–0.7 mm) was separated and used as starting material (sample AC0). Activated carbons were modified using chemical and thermal treatments, in order to obtain supports with different surface chemistries. Iron was then supported on these modified activated carbons by incipient wetness impregnation.

6.2.1.2 Oxidation with nitric acid in liquid phase

The starting activated carbon (sample AC0) was oxidized with HNO_3 using a 125 mL Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. A volume of 250 mL of 6 M HNO_3 was introduced into a 500 mL Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The oxidized activated carbon was extensively washed with distilled water to neutral pH and then dried in an oven at 110 ºC for 24 h (sample AC1) (Pereira et al., 2003).

6.2.1.3 Thermal treatment in gas-phase

Sample AC1 was the starting material for the preparation of other samples by gas-phase thermal treatments. The starting material had a large amount of oxygen surface groups that were selectively removed in different amounts (and types) by applying different temperatures. Samples AC1_400 ºC, AC1_700 ºC and AC1_900 ºC were obtained by heat treatment of AC1 under a flow of N_2 at 100 cm^3 min^{-1} for 1 h at 400 ºC, 700 ºC and 900 ºC, respectively, followed by treatment under dry air flow at room temperature for 1 h. The final treatment in dry air is intended to stabilize the surface chemistry of the samples (Pereira et al., 2003).

6.2.1.4 Preparation of catalysts

The active metal was supported on activated carbons by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under vacuum and ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110 ºC for 24 h, heat-treated under a nitrogen flow at 400 ºC for 1 h, and finally reduced at 400 ºC in hydrogen flow for 3 h (sample ZVI/support). The iron load was maintained constant at 3 wt%. The treatment methods for the activated carbon used in this work are summarized in Table 6.1.

Table 6.1 Abbreviations and description of original, modified and iron supported activated carbons

Abbreviation	**Description**
AC0	Untreated AC
AC1	HNO_3-treated AC0
AC1_400 ºC	Heat-treated AC1 under N_2 flow at 400ºC
AC1_700 ºC	Heat-treated AC1 under N_2 flow at 700ºC
AC1_900 ºC	Heat-treated AC1 under N_2 flow at 900ºC
ZVI/ACx-y	Iron impregnated on ACx-y

x-y: represents the modification undergone on activated carbon.

6.2.2 Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196 ºC, temperature programmed desorption (TPD), and by determination of the pH at the point of zero charge (pH_{PZC}). The catalysts were also analyzed by temperature programmed reduction (TPR).

6.2.2.1 Textural characterization

The textural characterization of the supports and catalyst was based on the N_2 adsorption isotherms, determined at -196 ºC with a Quanthachrome NOVA 4200e equipment. Prior to the measurements, the samples were outgassed at 120 ºC for 5 h under vacuum. The surface area (S_{BET}) of the samples was calculated by the B.E.T. method, and the specific surface area of the mesopores (S_{meso}) and micropore volume (V_{micro}) were calculated by the t-method.

6.2.2.2 Surface chemistry characterization

The surface chemistry of the activated carbons was characterized by temperature-programmed desorption (TPD) (Pereira et al., 2003). The TPD spectra of CO and CO_2 were obtained with a fully automated AMI-300 (Altamira instruments). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 1100 ºC under a constant flow rate of He at 25 cm^3 min^{-1}. The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the carbon samples were monitored with a mass spectrometer (Dymaxion, Ametek). CO and CO_2 were calibrated at the end of each analysis.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH (Órfão et al., 2006).

6.2.2.3 Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) analysis allows finding the most appropriate reduction temperature of the metal and to evaluate the effect of modified activated carbons on the metal reducibility. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The sample (0.15 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 ºC min^{-1} up to 600 ºC under a flow of 5% (v/v) H_2 in Ar at 30 cm^3 min^{-1}. The H_2 consumption was monitored by a thermal conductivity detector (TCD). The temperature range where reduction occurs could be indicated directly from the H_2 consumption peaks.

6.2.3 Batch adsorption and catalytic tests

Adsorption and CWPO experiments were carried out in a magnetically stirred batch reactor. The reactor was filled with 100 mL of a phenol aqueous solution (150 mg/L) and heated by immersion in a water bath at controlled temperature (30 ºC). The solution pH was adjusted to a value of 3.0 using H_2SO_4 solution (1 M). A calculated volume of H_2O_2 (0.25 mL) was added into the system after catalyst addition (100 mg), in order to reach a H_2O_2 concentration of 750 mg/L in the CWPO runs (the theoretical stoichiometric amount needed to completely mineralize phenol); at this moment the reaction was assumed to start. The CWPO oxidation runs were carried out both using the activated carbons (without iron) and iron supported carbons as catalysts, in order to evaluate the ability of the supports alone to decompose H_2O_2, and subsequently to promote phenol oxidation. This may give an idea to discriminate between a potential catalytic surface chemistry effect and the catalytic activity owing to the presence of iron.

Pure adsorption runs were performed in order to assess the contribution of adsorption to the removal of phenol. The experiments were carried out in the same conditions, but without H_2O_2 addition.

Adsorption and CWPO triplicate experiments showed relative errors lower than ±2%.

6.2.4 Analytical methods

Liquid samples were periodically withdrawn from the reactor for both adsorption and CWPO tests. Then, each sample was filtered with a syringe filter of 0.20 µm nylon (Teknokroma, ref._TR-200101) and placed in a glass vial (Agilent) for immediate analysis.

The phenol concentration was determined in a High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were carried out with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL.

Total Organic Carbon (TOC) was also determined at the end of the experiments in a TC Multi Analyzer 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector.

Fe leached to the reaction media was determined by using Atomic Absorption Spectroscopy (AAS) at 249 nm.

The main parameters used to compare the results in the discussion section are the removal of phenol (X_{PhOH}) and TOC abatement (X_{TOC}), which are respectively defined as:

$$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \qquad (6.1)$$

where $[PhOH]_0$ is the initial phenol concentration and $[PhOH]_t$ is the concentration at time t, and

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \tag{6.2}$$

where TOC_0 is the initial TOC concentration and TOC_t is the concentration at time t.

6.3 Results and discussion

6.3.1 Characterization of activated carbons and catalysts

6.3.1.1 Textural properties

Table 6.2 summarizes the textural properties of the different AC supports and ZVI/AC0 catalyst. As expected, the oxidation and thermal treatments have no significant impact on the textural properties of the materials. The slight decrease in AC1 surface area may be due to the high amount of oxygen-containing groups introduced on the AC0 surface with HNO_3 treatment, which possibly block the entry of N_2 molecules inside the small pores (Rodrigues et al., 2011).

Table 6.2 Textural properties of samples

Sample	**S_{BET} (m^2 g^{-1})**	**S_{meso} (m^2 g^{-1})**	**V_{micro} (cm^3 g^{-1})**
AC0	984	207	0.351
AC1	853	141	0.342
AC1_400 ºC	976	193	0.363
AC1_700 ºC	1020	200	0.371
AC1_900 ºC	1011	184	0.372
ZVI/AC0	975	216	0.348

On the contrary, there is a small increase of the surface area and micropore volume of the heat treated samples when compared to the sample oxidized with HNO_3 (AC1) due to the removal of the oxygen-containing functional groups on the activated carbon surface by thermal decomposition (Tangsathitkulchai et al., 2009).

The textural parameters of the ZVI/AC0 catalyst are not significantly different from the unsupported carbon (AC0) according to the values in Table 6.2. Therefore, it was assumed that the surface areas of the modified supports and the supported metal catalysts are not significantly different from the original support.

6.3.1.2 Surface chemistry characterization

The surface oxygenated groups on carbon materials can be determined from TPD spectra, since these surface groups (carboxylic acids, carboxylic anhydrides, lactones, phenols, and carbonyls or quinones) decompose upon heating in an inert atmosphere, releasing CO and CO_2 at different temperatures (Pereira et al., 2003; Figueiredo et al., 2007). Accordingly, it is possible to identify and estimate the amount of the oxygenated groups on a given material by TPD experiments. The nature of the groups can be assessed by the decomposition temperature and the type of gas released, and their respective amounts determined by the areas of the component peaks, obtained by deconvolution techniques (Pereira et al., 2003; Figueiredo et al., 2007). It was reported that CO_2 peak result from the decomposition of carboxylic acids at lower temperatures (from 200 to 450 ºC), or lactones at high temperatures (from 550 to 700 ºC); carboxylic anhydrides originate both CO and CO_2 (from 450 to 650 ºC); groups such as phenols (from 600 to 850 ºC) and carbonyls/quinones (from 800 to 1000 ºC) are CO evolving groups (Pereira et al., 2003; Figueiredo et al., 2007).

Figure 6.1 shows the TPD spectra (evolution of CO and CO_2) of the carbon samples. As clearly seen, the original AC does not have important amounts of oxygenated surface groups. The amounts of CO (Figure 6.1a) and CO_2 (Figure 6.1b) released from sample AC1 are considerably higher than those released from sample AC0, demonstrating the effect of the oxidation treatment with HNO_3. After the heat treatment at different temperatures under N_2 flow, it can be observed that the CO_2 and CO releasing groups have been selectively removed from the carbon surface; higher amounts of surface groups were removed at higher temperatures. For instance, after heat treatment at 900 ºC, no significant oxygenated groups remained on the carbon surface.

The deconvolution of the CO and CO_2 spectra was carried out in order to determine the amount of each surface group. A multiple Gaussian function was used for fitting each spectrum. The numerical calculations were based on a non-linear routine, which minimized the sum of squared deviations, using the Levenberg-Marquardt method to perform the iterations and some assumptions according to previous literature (Pereira et al., 2003; Figueiredo et al., 2007).

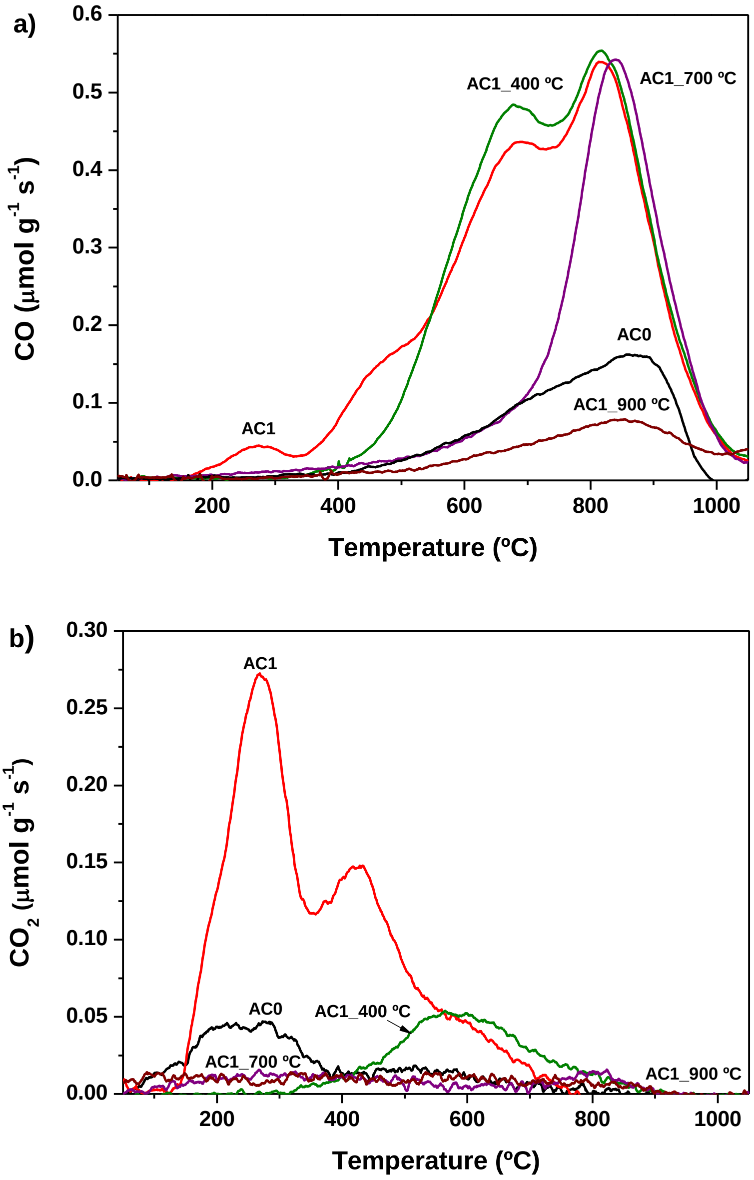

Figure 6.1 TPD spectra of the different carbon samples: (a) CO and (b) CO_2 evolution

Table 6.3 shows the amounts of the oxygenated groups, total CO and CO_2 released and pH_{PZC} of the carbon samples. The treatment with HNO_3 originates a large amount of surface oxygenated groups, which is evidenced by the increase of CO and CO_2 released as observed in Figure 6.1. This results from the decomposition of carboxylic acid groups (CO_2 released from 200 to 450 ºC), and in less extent carboxylic anhydrides (CO and CO_2

released from 450 to 650 ºC) and lactones (CO_2 released from 550 to 700 ºC). High amounts of phenols and carbonyl/quinone groups (CO released at high temperatures) were also introduced by this treatment. As expected, the oxidized sample AC1 has a low pH_{PZC} (Table 6.3) due to the introduction of oxygen-containing groups on the carbon surface with acidic characteristics, namely carboxylic acids. This sample also presents the lowest ratio CO/CO_2, indicating that this sample is the most acidic.

Both Figure 6.1 and Table 6.3 illustrate that thermal treatments selectively remove the surface groups introduced by the oxidation with HNO_3, and originating materials with progressively lower oxygen content. It can also be seen in Table 6.3 that the amount of acidic groups considerably decreases after thermal treatments above 400 ºC; on the other hand, phenols and carbonyls/quinones only decrease significantly after heat treatment above 700 ºC. Almost all oxygenated groups are removed at 900 ºC. As can be seen in the TPD spectra, practically all CO and CO_2 releasing groups were removed from sample AC1_900 ºC, which shows basic properties giving the highest pH_{PZC} value (Menendez et al., 1996). This basic character is mainly due to the electron rich oxygen-free sites located on the carbon basal planes, as reported by Leon y Leon et al. (Leon y Leon et al., 1992) The heat treated samples presents the highest CO/CO_2 ratio, indicating their less acidic characteristics. The basic nature of the samples increases with the temperature of thermal treatment, due to the fact that acid groups are removed at lower temperatures than the neutral and basic groups. The pH_{PZC} values are consistent with the TPD data.

Table 6.3 Chemical characterization of the activated carbon supports (obtained by deconvolution of CO and CO_2 TPD spectra) and pH_{PZC}

Sample	Carboxylic acids (µmol g^{-1})	Carboxylic anhydrides (µmol g^{-1})	Lactones (µmol g^{-1})	Phenols (µmol g^{-1})	Carbonyl/ Quinones (µmol g^{-1})	CO (µmol g^{-1})	CO_2 (µmol g^{-1})	pH_{PZC}
AC0	110	36	18	228	306	598a	164	6.7
AC1	378	288	88	815	1130	2311[a]	754	2.5
AC1_400 ºC	0	36	95	1068	1104	2244[a]	131	6.3
AC1_700 ºC	0	48	34	183	1080	1311	82	7.5
AC1_900 ºC	0	16	0	84	252	352	16	8.9

[a] The total amount of CO is slightly higher than the sum of the groups that decompose releasing CO. The justification can be found in (Figueiredo et al., 2007)

6.3.1.3 TPR

TPR profiles of the ZVI catalysts supported on the different carbon samples are shown in Figure 6.2. As it can be seen, the position, width and intensity of the iron reduction peaks mainly depend on the nature of the supports. Figure 6.2 shows that the major reduction peak is located at a temperature around 400 ºC for original (AC0) and oxidized AC (AC1). When AC1 is used as a support, a wide reduction peak was observed, this could be related to a higher interaction between iron and the oxygen-containing surface groups formed during the oxidation treatment with HNO_3, mainly carboxylic acid (Soares et al., 2010).

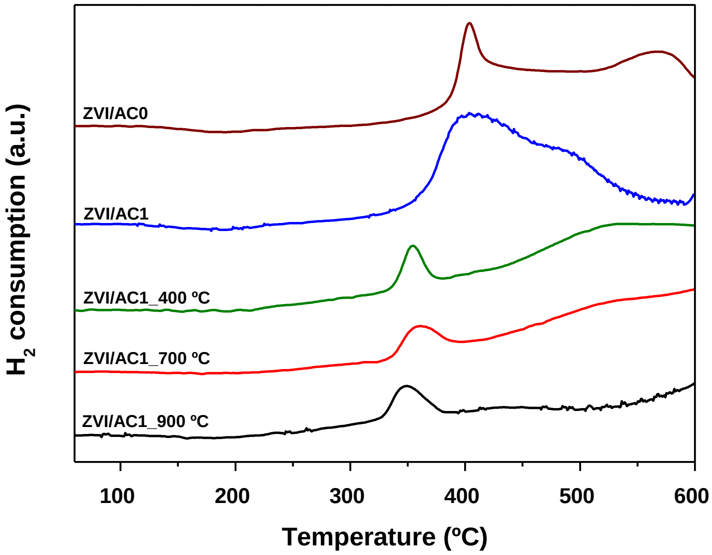

Figure 6.2 TPR profiles of iron supported on the carbon samples

On the other hand, the TPR profiles of the heat-treated samples present a reduction peak displaced to the left, corresponding to a decrease of the reduction temperature to around 350 ºC. The intensity of the reduction peak also decreased with the increase of the heat treatment temperature, which must be associated with the lower amount of surface groups of the support. This means that the reduction temperature of iron depends on the degree of interaction with the support.

6.3.2 Catalytic activity

The phenol removal on the original and modified activated carbons was studied as a function of time under the following conditions: 100 mL of solution having 150 mg/L of phenol, adsorbent/catalyst amount = 1 g/L, initial pH of the solution = 3.0, T = 30 ºC, atmospheric pressure and stoichiometric amount of H_2O_2 (750 mg/L).

6.3.2.1 Adsorption experiments

Adsorption experiments were performed for activated carbons and ZVI catalysts to evaluate the effect of the surface chemistry of carbon samples on phenol adsorption. Figure 6.3 shows phenol removal by adsorption against time for the activated carbon samples. The results indicate that the phenol adsorption capacity increases as the temperature of the thermal treatment increases. From the data listed in Table 6.2, it can be seen that there are not important differences between the textural properties of all the samples. Therefore, the difference in adsorption capacities must be mainly attributed to the different surface oxygen contents of the carbon samples.

The best phenol adsorption performances were observed for both AC1_700 ºC and AC1_900 ºC samples, reaching values of 68% and 75%, respectively after 3 h. Coughlin and Ezra (Coughlin and Ezra, 1968) suggested that the phenol adsorption is governed by $\pi-\pi$ dispersive interactions between electrons in the basal plane of carbon and electrons of the aromatic ring of phenol. As the temperature of treatment increases, the oxygen-containing surface groups are progressively removed, decreasing the surface oxygen content, thereby favoring those interactions (Moreno-Castilla et al., 1995). Even though the difference is not large, heat treated activated carbon at 900 ºC (sample AC1_900 ºC) improves the adsorption capacity of AC0.

On the contrary, phenol removal for acidic samples (AC1 and AC1_400 ºC) was lower and similar for both samples, reaching only about 45% in 3 h, since both had the highest amount of oxygenated surface groups (Table 6.3). The presence of these groups, most of them having electron – withdrawing properties, decreases the electronic density on the carbon basal planes, which should lead to weaker π-π dispersive interactions. In addition, there is competition between water and phenol molecules. Water can form hydrogen bonds with the hydrophilic oxygenated groups on the carbon surface, originating clusters that may hinder or even block the passage of phenol molecules to the surface. Such phenomenon was already reported (Bandosz et al., 1993; Karanfil and Kilduff, 1999; Franz et al., 2000; Villacañas et al., 2006; Faria et al., 2008) in adsorption studies of organic compounds, namely aromatics.

Phenol removal by adsorption on the ZVI catalysts was similar to those obtained in the presence of the corresponding supports. This was expected, since the textural properties of the ZVI catalysts supported on activated carbons are not significantly different from the corresponding unloaded carbons.

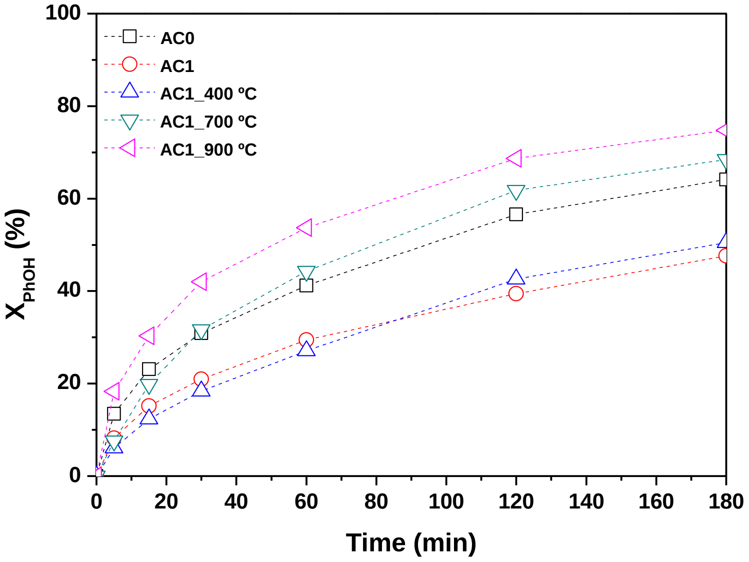

Figure 6.3 Phenol removal obtained in pure adsorption experiments (150 mg/L of phenol, pH 3.0, T = 30 ºC and adsorbent load = 1 g/L) with different carbon supports

6.3.2.2 CWPO experiments

Activated carbons as catalysts: Before comparing the performance of all the iron supported catalysts in the CWPO of phenol, it is important to evaluate the potential catalytic activity of the activated carbon samples used as support. For that reason, several experiments were performed under the same conditions as the adsorption tests, but adding H_2O_2. The corresponding phenol removal profiles are shown in Figure 6.4.

Phenol removals by CWPO in the presence of the activated carbon supports as catalysts were slightly higher than those obtained by adsorption on the corresponding samples. For instance, the phenol removal at 120 min for AC1_900 ºC is 69% without H_2O_2 and 72% in the presence of H_2O_2, or 72% and 78%, respectively, at 180 min, which suggests that the phenol disappearance is governed by adsorption. The results of phenol removal by adsorption (Figure 6.3) and CWPO (Figure 6.4) lead to the conclusion that the carbon materials as catalysts are not particularly active for CWPO of phenol; rather the removal of phenol is mainly due to pure adsorption. This is in agreement with the results reported (Taran et al., 2010) for other organic contaminants in the presence of modified carbons.

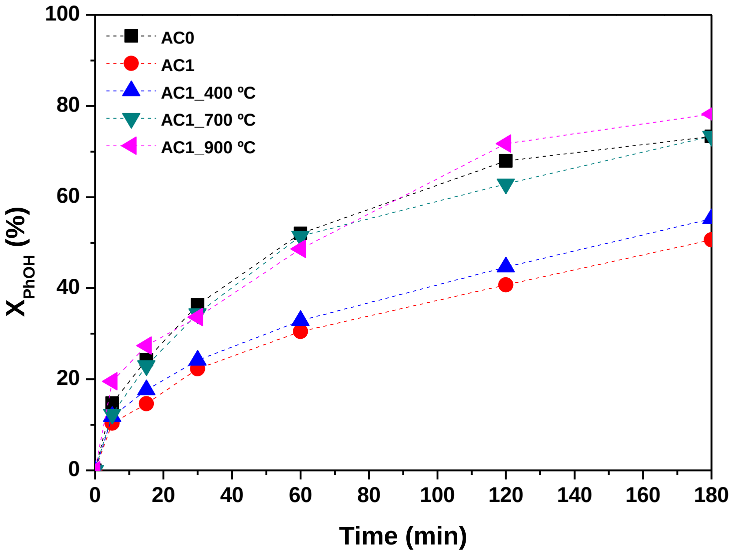

Figure 6.4 Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and activated carbon load = 1 g/L) with different carbon supports

Iron supported catalysts: In order to study the influence of the surface chemistry of the support on the activity of iron catalysts (ZVI) in phenol oxidation, a set of runs were performed in CWPO conditions. Figure 6.5 shows the results of phenol removal obtained with the supported ZVI catalysts. As expected, the presence of ZVI in all carbon supports improved the phenol removal efficiency, irrespective of their surface chemistry. However, ZVI supported on basic supports (ZVI/AC1_900 ºC, ZVI/AC1_700 ºC and ZVI/AC0) show a better performance, allowing to reach above 85% phenol conversion after 3 h, when compared to the obtained using iron supported on acidic supports (AC1 and AC1_400 ºC).

As it can be observed in Figure 6.3 and other studies (Vleeming et al., 1997), the presence of surface groups can cause differences in adsorption performance. In conclusion, the results suggest that surface acid groups are not favorable for adsorption and subsequent oxidation of phenol. In contrast, basic carbons, which contain a high content of electron rich sites on their basal planes, facilitate adsorption of phenol and subsequent degradation in the presence of ZVI and hydrogen peroxide. This can be explained by the synergetic effect of the basic surface groups and iron on the surface of carbon samples, promoting phenol oxidation. In this case, the access of H_2O_2 to iron could be easier than for the other samples with more oxygenated surface groups, and accelerates the hydroxyl radical generation for the oxidation of phenol.

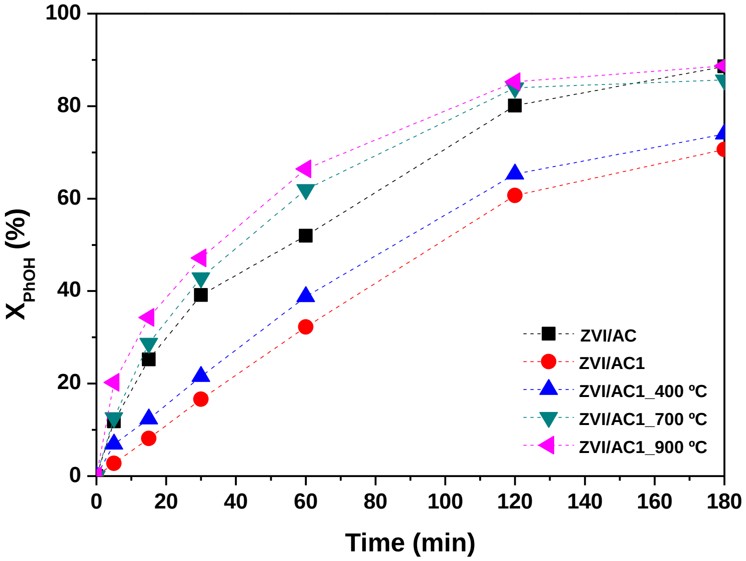

Figure 6.5 Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) with ZVI supported on different carbon samples

Table 6.4 shows the TOC removal at the end of adsorption and oxidation tests using carbon samples and ZVI supported on activated carbons. The results show that the support containing higher amounts of surface oxygenated acidic groups (AC1 and AC1_400 ºC) present lower TOC removal performance for both in the adsorption and oxidation tests when these materials were used as adsorbents or catalysts, respectively. Although, ZVI supported catalysts on these supports (AC1 and AC1_400 ºC) promote the TOC removal, it is still low compared to other supports. In fact, basic oxygen-free supports (AC, AC1_700 ºC and AC1_900 ºC) show better TOC removal, either in adsorption or oxidation conditions. It is also observed that the TOC removal attained with the ZVI supported catalysts follows the same tendency as the activity found for the phenol removal, i.e., AC1_900 ºC ≥ AC1_700ºC > AC0 > AC1_400 ºC> AC1, thus allowing to conclude that HNO_3 treatment decrease the activity of the original AC while the absence of acidic oxygenated groups on the surface of the carbon samples will slightly benefit the reaction.

Leaching tests were performed after 180 min of reaction, in order to evaluate the stability and contribution of homogeneous reaction for each catalyst. Leaching of iron corresponds to values below 0.04% of the metal initially present in almost all catalysts. In conclusion, the contribution of homogeneous catalysis is negligible, as the amount of leached iron is quite low.

Table 6.4 TOC removal after 180 min obtained in adsorption and CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and adsorbent/catalyst load = 1 g/L) with carbon samples and ZVI supported on activated carbons

Sample	**X_{TOC} (%)**		
	Adsorption by supports	**CWPO by supports**	**CWPO by ZVI/supports**
AC0	63	65	69
AC1	48	52	55
AC1_400 ºC	55	59	63
AC1_700 ºC	71	73	76
AC1_900 ºC	73	74	76

6.4 Conclusions

The adsorption performance of the activated carbons and the catalytic activity of ZVI for phenol removal depend on the concentration of oxygen-containing species on the carbon surface. Phenol removal by adsorption for acidic samples was lower since they had the highest amount of surface oxygenated groups compared to other samples. As the temperature of the heat treatment increases, the oxygen-containing surface groups in the carbon surface are progressively removed, decreasing the surface oxygen content, thereby favoring the interaction between the π-electron system of the basal planes of AC and the phenolic aromatic rings, and thus increasing the adsorption capacity of phenol on the surface.

Phenol removal by CWPO in the presence of the activated carbon samples as catalysts was slightly higher than those obtained by adsorption. Thus, these carbon materials in the absence of iron are not particularly active for CWPO of phenol; hence, the removal of phenol is mainly due to pure adsorption.

The presence of ZVI in all the carbon supports improved the phenol removal efficiency, irrespective of their surface chemistry. However, ZVI supported on basic activated carbons (ZVI/AC1_900 ºC, ZVI/AC1_700 ºC and ZVI/AC0) show a better performance, allowing above 85% phenol conversion after 3 h, compared to those obtained using catalysts supported on acidic carbon materials.

The TOC removal performance is higher either in the adsorption or oxidation tests when the support contains lower amounts of surface oxygenated acidic groups. Moreover, the leaching is below 0.04% of the metal initially present after 180 min of reaction in almost all catalysts.

References

Bandosz, T.J.; Jagiello, J.; Schwarz, J.A., Effect of Surface Chemical Groups on Energetic Heterogeneity of Activated Carbons, Langmuir 9 (1993) 2518–2522.

Bremner, D.H.; Burgess, A.E.; Houllemare, D.; Namkung, K.C., Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, Appl. Catal. B: Environ. 63 (2006) 15–19.

Coughlin, R.W.; Ezra, F.S., Role of surface acidity in the adsorption of organic pollutants on the surface of carbon, Environ. Sci. Technol. 2 (1968) 291–297.

Faria, P.C.C.; Órfão, J.J.M.; Figueiredo, J.L., Pereira, M.F.R., Adsorption of aromatic compounds from the biodegradation of azo dyes on activated carbon, Appl. Surf. Sci. 254 (2008) 3497–3503.

Figueiredo, J.L.; Pereira, M.F.R., in: Serp, P.; Figueiredo, J.L. (Eds.), Carbon Materials for Catalysis, John Wiley & Sons, Inc., Hoboken, NJ, 2009, pp. 177–217.

Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.M.A.; Órfão, J.J.M., Characterization of active sites on carbon catalysts, Ind. Eng. Chem. Res. 46 (2007) 4110–4115.

Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.M.A.; Órfão, J.J.M., Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.

Fortuny, A.; Font, J.; Fabregat, A., Wet air oxidation of phenol using active carbon as catalyst, Appl. Catal. B: Environ. 19 (1998) 165–173.

Franz, M.; Arafat, H.A.; Pinto, N.G., Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon, Carbon 38 (2000) 1807–1819.

Guélou, E.; Barrault, J.; Fournier, J.; Tatibouët, J.M., Active iron species in the catalytic wet peroxide oxidation of phenol over pillared clays containing iron, Appl. Catal. B: Environ. 44 (2003) 1–8.

Kang, S.F.; Liao, C.H.; Chen, M.C., Preoxidation and coagulation of textile wastewater by the Fenton process, Chemosphere 46 (2002), 923–928.

Karanfil, T.; Kilduff, J.E., Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 1. Priority pollutants, Environ. Sci. Technol. 33 (1999) 3217–3224.

Klavarioti, M.; Mantzavinos, D.; Kassinos, D., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.

Leon y Leon, C.A.; Solar, J.M.; Calemma, V.; Radovic, L.R., Evidence for the protonation of basal plane sites on carbon, Carbon 30 (1992) 797–811.

Liou, R.M.; Chen, S.H.; Hung, M.Y.; Hsu, C.S.; Lai, J.Y., Fe (III) supported on resin as effective catalyst for the heterogeneous oxidation of phenol in aqueous solution, Chemosphere 59 (2005) 117–125.

Matatov-Meytal, Y.I.; Sheintuch, M., Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309–326.

Menendez, J.A.; Phillips, J.; Xia, B.; Radovic, L.R., On the modification and characterization of chemical surface properties of activated carbon: In the search of carbons with stable basic properties, Langmuir 12 (1996) 4404–4410.

Moreno-Castilla, C.; Rivera-Utrilla, J.; López-Ramón, M.V.; Carrasco-Marín, F., Adsorption of some substituted phenols on activated carbons from bituminous coal, Carbon 33 (1995) 845–851.

Nayak, P.S.; Singh, B.K., Removal of phenol from aqueous solutions by sorption on low cost clay, Desalination 207 (2007) 71–79.

Órfão, J.J.M.; Silva, A.I.M.; Pereira, J.C.V.; Barata, S.A.; Fonseca, I.M.; Faria, P.C.C.; Pereira, M.F.R., Adsorption of a reactive dye on chemically modified activated carbons–Influence of pH, J. Colloid Interface Sci. 296 (2006) 480–489.

Paisio, C.E.; Agostini, E.; González, P.S.; Bertuzzi, M.L., Lethal and teratogenic effects of phenol on Bufo arenarum embryos, J. Hazard. Mater. 167 (2009) 64–68.

Pereira, M.F.R.; Órfão, J.J.M.; Figueiredo, J.L., Influence of the textural properties of an activated carbon catalyst on the oxidative dehydrogenation of ethylbenzene, Colloids Surf. A: Physicochem. Eng. Aspects 241 (2004) 165–171.

Pereira, M.F.R.; Soares, S.F.; Órfão, J.J.M.; Figueiredo, J.L., Adsorption of dyes on activated carbons: influence of surface chemical groups, Carbon 41 (2003) 811–821.

Pérez, M.; Torrades, F.; García-Hortal, J.A.; Doménech, X.; Peral, J., Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Appl. Catal. B: Environ. 36 (2002) 63–74.

Pignatello, J.J.; Oliveros, E.E.; Mackay, A., Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Environ. Sci. Technol. 36 (2006) 1–84.

Quintanilla, A.; Casas, J.A.; Rodriguez, J.J.; Kreutzer, M.T.; Kapteijn, F.; Moulijn, J.A., Kinetics of the wet oxidation of phenol over an Fe/Activated carbon catalyst, Int. J. Chem. Reactor Eng. 5 (2007) A62.

Rey, A.; Faraldos, M.; Casas, J.A.; Zazo, J.A.; Bahamonde, A.; Rodríguez, J.J., Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, Appl. Catal. B: Environ. 86 (2009) 69–77.

Rivera-Utrilla, J.; Sánchez-Polo, M., Ozonation of 1,3,6-naphthalenetrisulphonic acid catalysed by activated carbon in aqueous phase, Appl. Catal. B: Environ. 39 (2002) 319–329.

Rodrigues, E.G.; Carabineiro, S.A.C.; Chen, X.; Delgado, J.J.; Figueiredo, J.L.; Pereira, M.F.R.; Órfão, J.J.M., Selective oxidation of glycerol catalyzed by Rh/activated carbon: importance of support surface chemistry, Catal. Lett. 141 (2011) 420–431.

Rodríguez-Reinoso, F., The role of carbon materials in heterogeneous catalysis, Carbon 36 (1998) 159–175.

Segura, Y.; Martínez, F.; Melero, J.A., Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron, Appl. Catal. B: Environ. 136-137 (2013) 64–69.

Segura, Y.; Martínez, F.; Melero, J.A.; Molina, R.; Chand, R.; Bremner, D.H., Enhancement of the advanced Fenton process (Fe^0/H_2O_2) by ultrasound for the mineralization of phenol, Appl. Catal. B: Environ. 113-114 (2012) 100–106.

Soares, O.S.G.P.; Órfão, J.J.M.; Pereira, M.F.R., Pd-Cu and Pt-Cu catalysts supported on carbon nanotubes for nitrate reduction in water, Ind. Eng. Chem. Res. 49 (2010) 7183–7192.

Stüber, F.; Font, J.; Fortuny, A.; Bengoa, C.; Eftaxias, A.; Fabregat, A., Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater, Top Catal., 33 (2005) 3–50.

Suarez-Ojeda, M.E.; Stüber, F.; Fortuny, A.; Fabregat, A.; Carrera, J.; Font, J., Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst, Appl. Catal. B: Environ. 58 (2005) 105–114.

Tangsathitkulchai, C.; Ngernyen, Y.; Tangsathitkulchai, M., Surface modification and adsorption of eucalyptus wood-based activated carbons: Effects of oxidation treatment, carbon porous structure and activation method, Korean J. Chem. Eng. 26 (2009)1341–1352.

Taran, O.; Polyanskaya, E.; Ogorodnikova, O.; Kuznetsov, V.; Parmon, V.; Besson, M.; Descorme, C., Influence of the morphology and the surface chemistry of carbons on their catalytic performances in the catalytic wet peroxide oxidation of organic contaminants, Appl. Catal. A: Gen. 387 (2010) 55–66.

Villacañas, F.; Pereira, M.F.R.; Órfão, J.J.M.; Figueiredo,J.L., Adsorption of simple aromatic compounds on activated carbons, J. Colloid Interface Sci. 293 (2006) 128–136.

Vleeming, J.H.; Kuster, B.F.M.; Marin, G.B., Effect of platinum particle size and catalyst support on the platinum catalyzed selective oxidation of carbohydrates, Catal. Lett. 46 (1997) 187–194.

Zazo, J.A.; Fraile, A.F.; Rey, A.; Bahamonde, A.; Casas, J.A.; Rodríguez, J.J., Optimizing calcination temperature of Fe/activated carbon catalysts for CWPO, Catal. Today 143 (2009) 341–346.

Zazo, J.A.; Casas, J.A.; Mohedano, A.F.; Rodríguez, J.J., Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst, Appl. Catal. B: Environ. 65 (2006) 261–268.

CHAPTER 7

Preparation of zero valent iron/carbon xerogel for catalytic wet peroxide oxidation of phenol [5]

Nitrogen-free carbon xerogels prepared at different pH and nitrogen-containing carbon xerogel materials from urea and melamine precursors were prepared and evaluated as adsorbents/catalysts in the removal of phenol. Then ZVI was supported on these prepared carbon xerogel materials and its activity was evaluated for phenol removal by adsorption and CWPO. The prepared samples were characterized by determining the N_2 adsorption isotherms at -196 ºC, the pH at the point of zero charge (pH_{PZC}) and the elemental analysis. The textural properties of the pure and nitrogen-containing carbon xerogels are strongly influenced by the pH of the preparation solution and precursor used. The presence of ZVI in all carbon xerogel supports improved the phenol removal efficiency. However, ZVI supported on urea and melamine treated carbon xerogel at pH of 5.3 (ZVI/CXU-5.3 and ZVI/CXM-5.3) show a good performance, reaching above 87% phenol conversion after 60 min of CWPO. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e. CXU-5.3 and CXM-5.3) shows low removal efficiency below 5% after 60 min. The presence of ZVI on N-containing catalysts yields a better phenol removal, reaching values over 93% after 3 h, especially for those carbon xerogels having high nitrogen content (ZVI/CXM-5.3 and ZVI/CXM-6.9).

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[5] S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Zero-valent iron supported on surface modified carbon xerogel as catalysts for the oxidation of phenol by Fenton-like system. Under preparation.

7.1 Introduction

Wastewater containing phenol is generated in many chemical, petrochemical and pharmaceutical process industries (Fortuny et al., 1999; Santos et al., 2002). Phenolic pollutants are toxic in nature and have a great risk to the environment, which can cause negative health effects in human and aquatic life. Thus, the removal of phenols from industrial aqueous effluents is of a great importance, and has been received particular attention in the last few decades. For this purpose, various methods have been investigated based on biological, physical or chemical treatments (Pera-Titus et al., 2004; Kujawski et al., 2004; Fang et al., 2006; Santos et al., 2006).

Advanced oxidation processes (AOPs) are successfully used for waste waters containing high concentration of highly toxic pollutants (Pérez et al., 2002). Fenton process (Fe^{2+}/H_2O_2) is considered as an industrially viable alternative mainly operating under relatively mild conditions using hydrogen peroxide as oxidant and iron as a catalyst in simple reactor configurations (Klavarioti et al., 2009). This system generates highly reactive hydroxyl radicals, which can non-selectively oxidize a wide range of pollutants (Li et al., 2012). The main drawback of this homogeneous catalytic technology is the need of acidic conditions for proper performance (Pignatello, 1992), and the subsequent formation of large amounts of iron sludge after neutralization, which needs costly separation steps. Therefore, an alternative solution is proposed to prepare a heterogeneous catalyst containing both the catalytic metal (iron) and N-functional groups on the surface of carbon xerogel.

Carbon xerogels present excellent properties, such as high porosity, conductivity, controllable average pore size and they can be prepared in any desired form (Mahata et al., 2007). Recently, many studies have been worldwide performed for carbon xerogels, exploring their use in applications such as adsorbents (Kadirvelu et al., 2008; Girgis et al., 2011) and catalysts (Moreno-Castilla et al., 2005). Carbon xerogels have also proved to be excellent alternatives to activated carbons in various processes (Job et al., 2006; Zubizarreta et al., 2008; Contreras et al., 2010). Ribeiro et al. (Ribeiro et al. 2012) studied activated carbon xerogels for the removal of the anionic azo dyes Orange II and Chromotrope 2R by adsorption and catalytic wet peroxide oxidation. The results obtained in these experiments showed that carbon xerogel materials with higher basicity exhibit better adsorption performances and possess significant catalytic activity for oxidation.

Modification of carbon xerogels by the introduction of nitrogen groups onto the surface of activated carbons has been investigated in order to improve catalytic and adsorption properties (Tamai et al., 2006; Seredych et al., 2008). The main objective for the introduction of nitrogen groups on porous carbons is to induce surface basicity, thereby enhancing the adsorption properties. Moreover, the presence of nitrogen atoms in the carbon matrix has been shown to enhance the catalytic activity of carbon materials in oxidation reactions (Strelko et al., 2000; Boehm, 2009).

We have recently reported on the use of N-containing activated carbon as supports for zero valent iron catalysts (Messele et al., 2014). In particular, we have observed that zero valent iron supported onto a N-containing carbon was more active for the catalytic wet peroxide oxidation of phenol than the zero valent iron supported on conventional activated carbon.

Therefore, the objective of the present study is to prepare pure carbon xerogels at two different pHs (5.3 and 6.9) and N-containing carbon xerogels using two different N-containing precursors, urea or melamine (for use as supports/catalysts). Later, they were iron impregnated and then their performances were evaluated on adsorption and wet peroxide oxidation of phenol.

7.2 Experimental

7.2.1 Materials

Analytical standard of phenol (99%) and sodium chloride (99%) were purchased from Panreac. Resorcinol (99%), formaldehyde (37 wt.% in water, stabilized by 10-15 wt.% methanol), nitric acid, (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30%wt), urea (98%), sodium hydroxide (≥97%), and iron nitrate nonahydrate (>98%) were purchased from Sigma Aldrich. Melamine (≥99%) was purchased from Fluka. All chemicals were used as received without further purification. Deionised water was used throughout the work.

7.2.2 Preparation of carbon xerogels

In order to obtain materials with different textural properties, two different mesoporous carbon xerogels were prepared at pH 5.3 and 6.9 by the conventional sol-gel method using the polycondensation of resorcinol and formaldehyde in a molar ratio of 1:2 (Job et al., 2004; Job et al., 2005; Mahata et al., 2008). Modification of carbon xerogels by the introduction of N-containing groups (using urea and melamine as precursors) at two different pHs was also carried out (Honória et al., 2009). The carbonization step was carried out at low temperature (450 ºC) for all materials, in order to not decompose the nitrogen groups found in modified carbon xerogels. Above 600 ºC only thermally stable nitrogen substituted for carbon in the ring system can occur (Pels et al., 1995; Biniak et al., 1997; Mangun et al., 2001). For this reason, we set the carbonization temperature at 450 ºC for better comparison among all the materials. More detailed procedures are described below.

7.2.2.1 Preparation of pure (nitrogen-free) carbon xerogels

A 25 g sample of resorcinol was first mixed with 40 mL of distilled water under magnetic stirring. After dissolution, the pH was increased close to the chosen value by addition of 1 M NaOH solution. Then, 34 mL of formaldehyde were added and the final pH was adjusted to 5.3 and 6.9. The gelation was carried out in an oil bath at 85 ºC for 3 days. Later, the gel was crushed in small pieces and dried in an oven for 4 days by slow increase of temperature in order to remove water (60 ºC, 80 ºC, 100 ºC and 120 ºC for each day, respectively). The dried gel was carbonized under nitrogen flow at 450 ºC using the following heating program: a 2 ºC min^{-1} rate from room temperature to 200 ºC (hold 2 h), then at 2 ºC min^{-1} up to 300 ºC (hold 1 h), later at 2 ºC min^{-1} up to 450 ºC (hold 2 h) and finally cooling down back to room temperature. The carbon xerogels prepared are referred to CX followed by the pH value, i.e., CX-5.3 and CX-6.9, respectively.

7.2.2.2 Preparation of nitrogen-containing carbon xerogels

Carbon xerogels containing N-functional groups were prepared using a procedure adapted from Sousa et al. (Sousa et al., 2012) A 15 g sample of resorcinol and 4 g of urea (or 3 g of melamine) were mixed in 18 mL of distilled water. The solution was heated up to 90 ºC under stirring until the urea (or melamine) was completely dissolved. Then, the solution was cooled to room temperature and 20 mL of formaldehyde were added. The pH was conveniently adjusted to 5.3 or 6.9. The gelling, drying and carbonization followed the same procedure described above, in section 7.2.2.1 The carbon xerogels were labeled as CXU or CXM based on the precursor used urea or melamine, respectively, followed by the pH value, i.e., CXU-5.3, CXU-6.9, CXM-5.3 and CXM-6.9.

7.2.2.3 Preparation of catalysts

Prior to use, all the carbon xerogels were grounded to 0.3-0.7 mm particle size. The active metal was supported on pure carbon xerogels and all the modified carbon xerogels by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110 ºC for 24 h and calcined under a nitrogen flow at 400 ºC for 1 h, then finally reduced at 400 ºC under hydrogen flow for 3 h (sample ZVI/support). The content of metal was maintained constant at 3 wt.%. Table 7.1 contains the description of all the prepared carbon xerogels.

Table 7.1 Abbreviations and description of the prepared carbon xerogels

Abbreviation	**Description**
CX-5.3	Carbon xerogel prepared at pH 5.3
CX-6.9	Carbon xerogel prepared at pH 6.9
CXU-5.3	Modified carbon xerogel with urea at pH 5.3
CXU-6.9	Modified carbon xerogel with urea at pH 6.9
CXM-5.3	Modified carbon xerogel with Melamine at pH 5.3
CXM-6.9	Modified carbon xerogel with Melamine at pH 6.9
ZVI/CXa	Iron impregnated on sample CXa

a: represents the preparation pH or modification undergone on the carbon xerogels

7.2.3 Characterization of carbon xerogel supports and catalysts

The textural characterization of the prepared carbon materials was determined by N_2 adsorption at -196 ºC with a Quantachrome NOVA 4200e multi-station instrument. The BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume (V_{micro}) were calculated using the BET equation and the t-method, respectively. The Barrett, Joyner and Halenda (BJH) method was used to calculate the average mesopore diameter.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH, and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH (Órfão et al., 2006).

Carbon, hydrogen, nitrogen and oxygen (by difference) contents were determined using a Carlo Erba EA 1108 Elemental Analyzer. Prior to the analysis, water adsorbed on the surface of the supports was removed by drying at 110 ºC in the oven overnight.

7.2.4 Adsorption and catalytic tests

The adsorption and CWPO experiments were carried out in a magnetically stirred tank (batch reactor). The reactor was filled with 100 mL of a phenol aqueous solution (150 mg/L) and heated by immersion in a water bath at controlled temperature. The solution pH was adjusted to a value of 3.0 using H_2SO_4 solution (1 M). When the desired temperature was reached (30 ºC), a calculated volume of H_2O_2 (0.25 mL) was added into the system after catalyst addition (100 mg), in order to reach a H_2O_2 concentration of 750 mg/L (the theoretical stoichiometric amount needed to completely mineralize phenol) in the CWPO runs; at this moment the reaction was assumed to start. The CWPO oxidation runs were carried out both using the carbon xerogels (without iron) and iron supported carbon xerogel as catalysts, in order to evaluate the ability of the supports alone to decompose H_2O_2, and subsequently to promote phenol oxidation. This may give an idea to discriminate between a potential catalytic surface chemistry and the catalytic activity owing to the presence of iron.

In addition, pure adsorption runs were performed in order to assess the contribution of adsorption to the removal of phenol. The experiments were carried out in the same conditions, but without H_2O_2 addition.

7.2.5 Analytical methods

Both in pure adsorption and in CWPO, liquid samples were periodically withdrawn from the reactor. Then, each sample was filtered with a syringe filter of 0.20 µm nylon (Teknokroma, ref._TR-200101) and placed in a glass vial (Agilent) for immediate analysis.

The determination of phenol concentration was performed by High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were carried out with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL.

Total Organic Carbon (TOC) was also determined at the end of the experiments in a TC Multi Analyzer 2100 N/C apparatus from Analytic Jena with a non-diffractive IR detector.

Fe leached from materials to the reaction media was determined by using Atomic Absorption Spectroscopy (AAS) at 249 nm.

The main parameters used to compare the results in the discussion section are the removal of phenol (X_{PhOH}) and TOC abatement (X_{TOC}), which are respectively defined as:

$$X_{PhOH}(\%)=\frac{[PhOH]_0-[PhOH]_t}{[PhOH]_0}\times 100 \tag{7.1}$$

where $[PhOH]_0$ is the initial phenol concentration and $[PhOH]_t$ is the concentration at time t, and

$$X_{TOC}(\%)=\frac{TOC_0-TOC_t}{TOC_0}\times 100 \tag{7.2}$$

where TOC_0 is the initial TOC concentration and TOC_t is the concentration at time t.

7.3 Results and discussion

7.3.1 Characterization of supports and catalysts

7.3.1.1 Textural properties

The textural properties of the pure and nitrogen-containing carbon xerogels are strongly dependent on the pH of the preparation solution and precursor used. Table 7.2 shows the textural parameters for all carbon xerogels studied. The BET surface area of the ZVI/CX-5.3 catalyst decreased only slightly compared to the unloaded carbon xerogel CX-5.3. Therefore, it was assumed that the textural properties of the supported zero valent iron catalysts are not significantly different from the corresponding supports.

Table 7.2 Textural properties and pH_{PZC} of supports and ZVI/CX-5.3 catalyst

Sample	**S_{BET} ($m^2\ g^{-1}$)**	**S_{meso} ($m^2\ g^{-1}$)**	**V_{micro} ($cm^3\ g^{-1}$)**	**V_{total} ($cm^3\ g^{-1}$)**	**pH_{pzc}**
CX-5.3	299	112	0.084	0.653	7.0
CX-6.9	16	16	0	0.013	6.8
CXU-5.3	35	16	0	0.014	6.1
CXU-6.9	406	131	0.127	0.748	6.6
CXM-5.3	0	0	0	0.020	6.4
CXM-6.9	375	106	0.122	0.207	6.2
ZVI/CX-5.3	292	75	0.081	0.646	-

In the case of pure carbon xerogel, a quite high S_{BET} of 299 $m^2\ g^{-1}$ and S_{meso} of 112 $m^2\ g^{-1}$ were found for the carbon xerogel synthesized at lower pH 5.3

(CX-5.3) compared to that of carbon xerogel synthesized at pH 6.9 (CX-6.9). Total pore volume in the case of the carbon xerogel synthesized at the lower pH, CX-5.3, is also noticeably greater, 0.653 cm^3 g^{-1}, than for the carbon xerogel synthesized at the higher pH CX-6.9, 0.013 cm^3 g^{-1}. The pH of the initial solution clearly plays a definitive role in the development of porosity and surface area. Thus, a slight pH increase led to an almost fifteen-fold lower pore volume and about 95% lower surface area. The main difference between CX-5.3 and CX-6.9 is the total pore volume and the surface area. According to the S_{meso} values, using a lower solution pH, a 7-fold increase in mesopores can be observed when compared CX-5.3 to CX-6.9.

In the case of the urea and melamine modified carbon xerogels, total pore volume and S_{BET} are significantly higher for the carbon xerogel synthesized at the higher pH of 6.9, irrespective of the nitrogen containing precursor. This means that nitrogen containing carbon xerogels synthesized at higher pH (CXU-6.9 and CXM-6.9) have higher specific surface area (S_{BET}) and total pore volume than that of nitrogen containing carbon xerogel synthesized at lower pH, CXU-5.3 and CXM-5.3. This shows that there is a development of the porosity of carbon xerogels prepared with urea and melamine as the pH increases. According to the pH_{PZC} values, all materials obtained have neutral or slightly basic properties, independently of the pH and nitrogen precursors used in their preparation.

7.3.1.2 Elemental analysis

The carbon, hydrogen, nitrogen and oxygen contents obtained by elemental analysis are summarized in Table 7.3. The nitrogen content of the pure carbon xerogels, CX-5.3 and CX-6.9 is very small (0.10%). As expected, significant amounts of nitrogen were introduced on the carbon xerogels synthesized with melamine (5.78–5.44%), compared to the carbon xerogels prepared with urea (3.31–3.17%).

Table 7.3 Elemental analysis of the carbon xerogels

Sample	**C (wt%)**	**H (wt%)**	**N (wt%)**	**O[a] (wt%)**
CX-5.3	80.40	2.74	0.10	16.77
CX-6.9	79.33	2.71	0.10	17.86
CXU-5.3	76.75	2.92	3.17	17.16
CXU-6.9	79.01	2.61	3.31	15.07
CXM-5.3	79.19	2.05	5.44	13.33
CXM-6.9	78.93	2.66	5.78	12.70

[a] oxygen determined by difference

The highest amount of nitrogen incorporated into the structure was obtained when melamine was the source of nitrogen, as its molecule contains up to six nitrogen atoms. Thus, the differences in the amounts of nitrogen may be directly related to the content of nitrogen in the precursors (67% in melamine and 47% in urea) (Seredych et al., 2008).

7.3.2 Adsorption and catalytic activity

The phenol removal on the pure an N-containing carbon xerogels was studied as a function of time under the following conditions: 100 mL of solution containing 150 mg/L of phenol, adsorbent or catalyst added at 1 g/L, initial pH of the solution set at 3.0, T = 30 ºC, atmospheric pressure, and the stoichiometric amount of H_2O_2 (750 mg/L) needed for total mineralization.

7.3.2.1 Adsorption experiments

Adsorption experiments were performed for carbon xerogels and ZVI catalysts to evaluate the effect of the surface chemistry and textural properties of carbon xerogel samples on phenol adsorption.

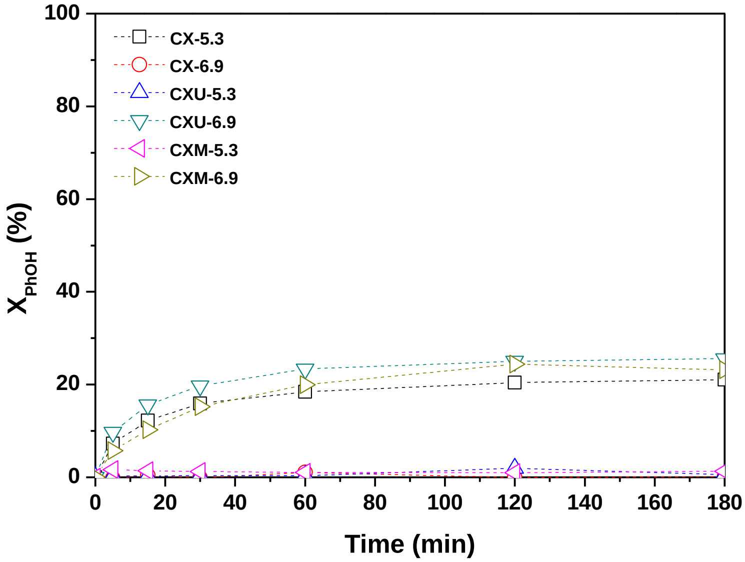

Figure 7.1 Phenol removal obtained in pure adsorption experiments (150 mg/L of phenol, pH 3.0, T = 30 ºC and adsorbent load = 1 g/L) with different carbon xerogel supports

Figure 7.1 shows phenol removal by adsorption against time for the carbon xerogel samples. In general, all the samples having higher surface area regardless of their surface chemistry, CX-5.3, CXU-6.9 and CXM-6.9, presented higher phenol adsorption capacity of 20% compared to those carbon xerogels having lower surface area, CX-6.9, CXU-5.3 and CXM-5.3, gives lower adsorption capacity of less than 1% in 60 min of adsorption. Therefore, the difference in adsorption capacities must be mainly attributed to the different textural properties of the carbon xerogel samples.

Phenol removal by adsorption on the ZVI catalysts was similar to those obtained in the presence of the corresponding supports (data not shown). This was expected, since the textural properties of the ZVI catalysts supported on activated carbons are not significantly different from the corresponding unloaded carbons.

7.3.2.2 CWPO experiments

Carbon xerogels as catalysts: In order to evaluate the potential catalytic activity of the carbon xerogel samples to act as catalysts (without any supported metal) in the CWPO of phenol, runs were performed under the same conditions as the adsorption tests but now adding H_2O_2. The corresponding phenol removal curves are shown in Figure 7.2.

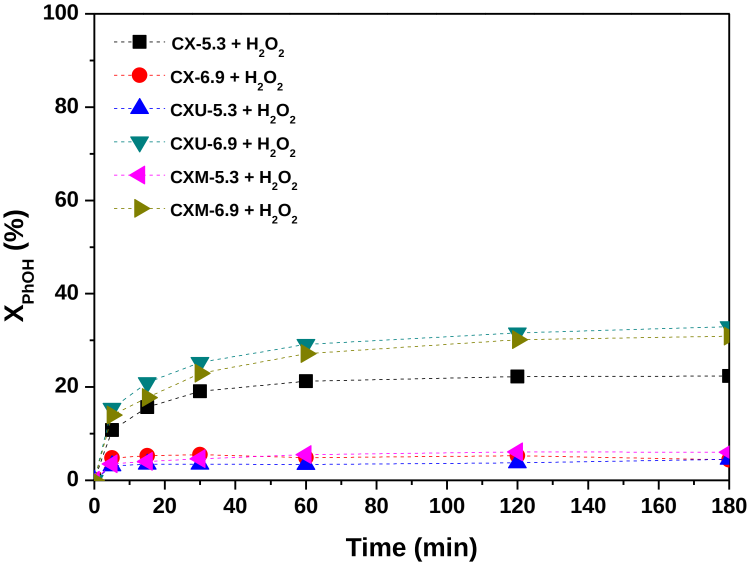

Figure 7.2 Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and activated carbon load = 1 g/L) with different carbon xerogel supports

Phenol removals by CWPO in the presence of the carbon xerogel supports as catalysts were slightly higher than those obtained by adsorption on the corresponding samples. For example, the phenol removal at 120 min for CXU-6.9 is 25% without H_2O_2 and 31% in the presence of H_2O_2, or 26% and 33%, respectively, at 180 min, which suggests that the phenol disappearance is governed by adsorption. The results of phenol removal by adsorption (Figure 7.1) and CWPO (Figure 7.2) lead to the conclusion that the carbon xerogel materials as catalysts are not particularly active for CWPO of phenol; rather the removal of phenol is mainly due to pure adsorption. Similar conclusion was obtained in a previous work for phenol in the presence of N-containing activated carbons (Messele et al., 2014).

Iron supported catalysts: To study the influence of the surface chemistry of the support on the activity of iron catalysts (ZVI) in phenol oxidation, a set of runs were performed in CWPO conditions. Figure 7.3 shows the results of phenol removal obtained with the supported ZVI catalysts. As expected, the presence of ZVI in all carbon xerogel supports improved the phenol removal efficiency. However, ZVI/CXU-5.3 and ZVI/CXM-5.3 show a good performance, reaching above 87% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e. CXU-5.3 and CXM-5.3) shows low removal efficiency below 5% after 60 min.

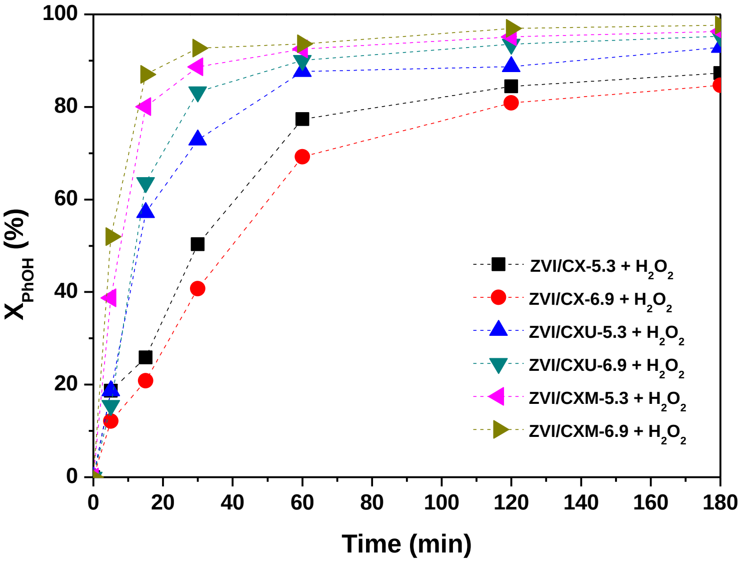

Figure 7.3 Phenol removal obtained in CWPO experiments (150 mg/L of phenol, H_2O_2 concentration of 750 mg/L, pH 3.0, T = 30 ºC and catalyst load = 1 g/L) with ZVI supported on different carbon xerogel samples

The presence of ZVI on N-containing catalysts yields a better phenol removal, reaching values over 93% after 3 h, especially for those carbon xerogels having high content of nitrogen (ZVI/CXM-5.3 and ZVI/CXM-6.9); the phenol removal efficiency is higher than the rest. These results revealed that there is a direct and positive relation between the catalytic activity and the nitrogen content of the materials. Therefore, the activity of iron supported catalysts based on N-containing carbon xerogel in CWPO of phenol is enhanced when compared to that of the pure carbon xerogels. It is thus observed that the presence of nitrogen groups on the surface of activated carbon, in addition to iron, clearly increases the phenol removal. This synergy can be probably assigned to the ability of retaining the iron ions close to the carbon surface due to the complexing properties of these N-containing groups as observed in the previous work (Messele et al., 2014).

7.4 Conclusions

Physical and chemical properties of nitrogen-doped xerogels depend on synthesis parameters and the type of nitrogen-containing precursor. The pH of the initial solution clearly plays a definitive roll in the development of porosity and surface area: a slight pH increase led to an almost fifteen-fold lower pore volume and about 95% lower surface area.

All the samples having higher surface area regardless of their surface chemistry, CX-5.3, CXU-6.9 and CXM-6.9, presented higher phenol adsorption capacity of 20% compared to those carbon xerogels having lower surface area, CX-6.9, CXU-5.3 and CXM-5.3, gives lower adsorption capacity of less than 1% in 60 min of adsorption. Therefore, the difference in adsorption capacities must be mainly attributed to the different textural properties of the carbon xerogel samples.

Phenol removals by CWPO in the presence of the carbon xerogel supports as catalysts were slightly higher than those obtained by adsorption on the corresponding samples. The results of phenol removal by adsorption and CWPO lead to the conclusion that the carbon xerogel materials as catalysts are not particularly active for CWPO of phenol.

The presence of ZVI in all carbon xerogel supports improved the phenol removal efficiency. However, ZVI/CXU-5.3 and ZVI/CXM-5.3 show a good performance, reaching above 87% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e. CXU-5.3 and CXM-5.3) shows low removal efficiency below 5% after 60 min.

References

Biniak, S.; Szymanski, G.; Siedlewski, J.; Swiatkowski, A., The characterization of activated carbons with oxygen and nitrogen surface groups, Carbon 35 (1997) 1799–1810.

Boehm, H.P., Catalytic properties of nitrogen-containing carbons. In: Serp P, Figueiredo JL, editors. Carbon materials for catalysis. Hoboken, NJ: Wiley; 2009 [Chapter 7, p. 219–65].

Contreras, M.S.; Paez, C.A.; Zubizarreta, L.; Leonard, A.; Blather, S.; Olivera Fuentes, C.G.; Arenillas, A.; Pirard, J.P.; Job, N., A comparison of physical activation of carbon xerogels with carbon dioxide with chemical activation using hydroxides, Carbon 48 (2010) 3157–3168.

Fang, H.H.P; Liang, D.W.; Zhang, T.; Liu, Y., Anaerobic treatment of phenol in wastewater under thermophilic condition, Water Res. 40 (2006) 427–434.

Fortuny, A.; Bengoa, C.; Font, J.; Castells, F.; Fabregat, A., Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, Catal. Today 53 (1999) 107–114.

Girgis, B.S.; Attia, A.A.; Fathy, N.A., Potential of nano-carbon xerogels in the remediation of dye-contaminated water discharges, Desalination 265 (2011) 169–176.

Gorgulho, H.F.; Gonçalves, F.; Pereira, M.F.R.; Figueiredo, J.L., Synthesis and characterization of nitrogen-doped carbon xerogels, Carbon 47 (2009) 2032–2039.

Job, N.; Théry, A.; Pirard, R.; Marien, J.; Kocon, L.; Rouzaud, J.N.; Béguin, F.; Pirard, J.P., Carbon aerogels, xerogels and cryogels: influence of the drying method on the textural properties of porous carbon materials, Carbon 43 (2005) 2481–2494.

Job, N.; Heinrichs, B.; Lambert, S.; Pirard, J.P.; Colomer, J.F.; Vertruyen, B.; Marien, J., Carbon xerogels as catalyst supports: study of mass transfer, AIChE J. 52 (2006) 2663–2676.

Job, N.; Pirard, R.; Marien, J.; Pirard, J.P., Porous carbon xerogels with texture tailored by pH control during sol–gel process, Carbon 42 (2004) 619–28.

Kadirvelu, K.; Goel, J.; Rajagopal, C., Sorption of lead, mercury and cadmium ions in multi-component system using carbon aerogel as adsorbent, J. Hazard. Mater. 153 (2008) 502–507.

Klavarioti, M.; Mantzavinos, D.; Kassinos, D., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.

Kujawski, W.; Warszawski, A.; Ratajczak, W.; Porebski, T.; Capała, W.; Ostrowska, I., Removal of phenol from wastewater by different separation techniques, Desalination 163 (2004) 287–296.

Li, W.; Nanaboina, V.; Zhou, Q.; Korshin, G.V., Degradation of pharmaceuticals and personal care products (PPCPs) in secondary wastewater by Fenton process, Water Res. 46 (2) (2012) 403–412.

Mahata, N.; Silva, A.R.; Pereira, M.F.R.; Freire, C.; de Castro, B.; Figueiredo, J.L., Anchoring of a [Mn(salen)Cl] complex onto mesoporous carbon xerogels, J. Colloid Interface Sci. 311 (2007) 152–158.

Mahata, N.; Pereira, M.F.R.; Suáez-García, F.; Martínez-Alonso, A.; Tascón, J.M.D.; Figueiredo, J.L., Tuning of texture and surface chemistry of carbon xerogels, J. Colloid Interface Sci. 324 (2008) 150–155.

Mangun, C.L.; Benak, K.R.; Economy, J.; Foster, K.L., Surface chemistry, pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia, Carbon 39 (2001) 1809–1820.

Messele, S.A.; Soares, O.S.G.P.; Órfão, J.J.M.; Stüber, F.; Bengoa, C.; Fortuny, A.; Fabregat, A.; Font, J., Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol, Appl. Catal. B: Environ. 154–155 (2014) 329–338.

Moreno-Castilla, C.; Maldonado-Hódar, F.J., Carbon aerogels for catalysis applications: an overview, Carbon 43 (2005) 455–465.

Órfão, J.J.M.; Silva, A.I.M.; Pereira, J.C.V.; Barata, S.A.; Fonseca, I.M.; Faria, P.C.C.; Pereira, M.F.R., Adsorption of a reactive dye on chemically modified activated carbons–Influence of pH, J. Colloid Interface Sci. 296 (2006) 480–489.

Pels, J.R.; Kapteijn, F.; Moulijn, J.A.; Zhu, Q.; Thomas, K.M., Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis, Carbon 33 (1995) 1641–1653.

Pera-Titus, M.; García-Molina, V.; Baños, M.A.; Giménez, J.; Esplugas, S., Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

Pérez, M.; Torrades, F.; García-Hortal, J.A.; Domènech, X.; Peral, J., Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Appl. Catal. B: Environ. 36 (2002) 63–74.

Pignatello, J.J., Dark and photoassisted Fe^{3+}-catlysed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol., 26 (1992) 944–951.

Rui, S.R.; Nady, A.F.; Amina, A.A.; Adrián, M.T.S.; Joaquim, L.F.; Helder T.G., Activated carbon xerogels for the removal of the anionic azo dyes Orange II and Chromotrope 2R by adsorption and catalytic wet peroxide oxidation, J. Chem. Eng. 195–196 (2012) 112–121.

Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, S.; García-Ochoa, F., Route of the catalytic oxidation of phenol in aqueous phase, Appl. Catal B: Environ. 39 (2002) 97–113.

Santos, A.; Yustos, P.; Gomis, S.; Ruiz, G.; Garcia-Ochoa, F., Reaction network and kinetic modeling of wet oxidation of phenol catalyzed by activated carbon, Chem. Eng. Sci. 61 (2006) 2457–2467.

Seredych, M.; Hulicova-Jurcakova. D.; Lu, G.Q.; Bandosz, T.J., Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance, Carbon 46 (2008) 1475–1488.

Sousa, J.P.S.; Pereira, M.F.R.; Figueiredo, J.L., NO oxidation over nitrogen doped carbon xerogels, Appl. Catal. B: Environ. 125 (2012) 398– 408.

Strelko, V.V.; Kuts, V.S; Thrower, P.A., On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbons in electron transfer reactions, Carbon 38 (2000) 1499–1524.

Tamai, H.; Shiraki, K.; Shiono, T.; Yasuda, H., Surface functionalization of mesoporous and microporous activated carbons by immobilization of diamine. J. Colloid Interface Sci. 295 (2006) 299–302.

Zubizarreta, L.; Arenillas, A.; Pirard, J.P.; Pis, J.J.; Job, N., Tailoring the textural properties of activated carbon xerogels by chemical activation with KOH, Microporous Mesoporous Mater. 115 (2008) 480–490.

CHAPTER 8

Conclusions and future work

The final chapter of this thesis presents a general overview of the main results, along with the most relevant conclusions. Finally, some ideas for future work are suggested.

8.1 Main Conclusions

Aqueous phase oxidation of phenol solutions (1000 mg/L) has been conducted from acidic up to circumneutral pH using classical Fenton system (Fe^{2+}/H_2O_2) with or without the addition of a chelating agent in order to enhance the oxidation performance. EDTA was selected for most of the tests under the same Fe^{2+} catalyst load (7 mg/L) and H_2O_2 dose (stoichiometric with respect to phenol).

In acidic conditions, close to the optimal pH (3-4), the presence of EDTA does not change the phenol conversion achieved under classical Fenton conditions, but, in excess of EDTA the phenol conversion becomes insignificant.

The phenol removal efficiency and peroxide decomposition rate significantly improved in presence of EDTA at near circumneutral pH. Over 95% of phenol conversion was obtained using an EDTA:Fe^{2+} ratio of 0.3:1 at pH 7.0, which is almost tenfold of that obtained in the absence of EDTA. Among the different EDTA:Fe^{2+} molar ratio tested, 0.3:1 ratio was found to be the optimum.

Other chelating agents, like EDDA, DTPA and NTA, demonstrated to enhance the oxidation ability of the Fenton system at neutral pH although EDDA provided the best oxidation performance.

Overall, the presence of a chelating agent in small quantities greatly broadens the pH range where the Fenton-like system is feasible, up to circumneutral pH. Thus, pH adjustment would not be required anymore or just limited for real caustic wastewaters, which can result in major saving of operational costs.

Later, nZVI/AC catalysts have been prepared and tested for CWPO of phenol in batch system. The SEM analyses indicated that nZVI were mostly found as clusters of aggregates of round-shaped particles and were loaded into the pores and cracks rather than onto outer surface. This interestingly allows the repeated use of the catalyst without noticeable loss of iron.

Phenol conversion above 90% can be reached using this catalyst (9 wt%) after only 15 min of reaction using the stoichiometric hydrogen peroxide for phenol concentrations in the range 150-1000 mg/L, which compares well with classical Fenton.

The recycling and consecutive reutilization of catalyst gave a final phenol removal nearly the same obtained with the fresh catalyst although at later time. The leaching observed is not excessive as it means less than 5% of the total initial iron in the catalyst even after 120 min of reaction, independently of the reactions conditions.

Activated carbons with different N-containing precursors were modified, characterized and tested as adsorbents or catalysts for adsorption and peroxide oxidation of phenol. Additionally, these modified carbons were also impregnated with iron (3 wt%) and used as catalysts for CWPO.

Treatments with EDA and melamine lead to a drastic surface area reduction. This may be due to the presence of numerous groups on the activated carbon surface. In the urea and EDA treated samples similar total contents of nitrogen are found regardless of the pretreatment applied. However, in the case of melamine treated samples, the nitrogen content is significantly higher. These materials are not particularly active for the reaction, the removal of phenol being mainly due to adsorption.

In turn, the iron supported catalysts based on N-containing AC show a high phenol removal efficiency, reaching values over 85% conversion after 3 h. This result revealed that there is a positive relation between the catalytic activity and the nitrogen content of the materials although its participation is not critical.

Regarding to oxygen functionalized activated carbons, the adsorption performance of the activated carbons and the catalytic activity of ZVI for phenol removal depend on the concentration of oxygen-containing species on the carbon surface. These activated carbon samples, in the absence of iron, are not particularly active for CWPO of phenol.

The presence of ZVI in all the carbon supports improved the phenol removal efficiency, irrespective of their surface chemistry. However, ZVI supported on basic activated carbons show a better performance, allowing above 85% phenol conversion after 3 h, compared to those obtained using catalysts supported on acidic carbon materials.

Physical and chemical properties of nitrogen-doped xerogels depend on synthesis parameters and the type of nitrogen-containing precursor. The pH of the initial solution clearly plays a definitive role in the development of porosity and surface area: a slight pH increase led to an almost fifteen-fold lower pore volume and about 95% lower surface area. In the absence of iron, the carbon xerogel materials are not particularly active for CWPO of phenol.

The presence of ZVI (3 wt%) in all the carbon xerogel supports improved the phenol removal efficiency. However, ZVI/CXU-5.3 and ZVI/CXM-5.3 show a good performance, reaching above 87% phenol conversion after 60 min. On the contrary, the phenol removal by pure adsorption and CWPO using the same material without the presence of ZVI (i.e. CXU-5.3 and CXM-5.3) shows low removal efficiency below 5% after 60 min.

8.2 Suggestions for future work

The results obtained and the conclusions derived must serve to design future research guidelines that would improve the knowledge gained in this thesis. Below, some observations about possible future research are given.

- It would be of interest in future investigations to assess the applicability of these materials (catalysts) for the removal of other refractory organic compounds.

- Another topic that needs to be further examined is to evaluate the feasibility of adding chelating ligands like EDTA in the homogeneous Fenton system.

- In this topic, several issues could be addressed, namely the identification of the oxidation by-products and evaluation of their potential toxicity.

- Also, as the presence of nitrogen groups over the activated carbon surface does not act as free chelating agents, the simultaneous use of nZVI/AC heterogeneous catalyst and a chelating agent in solution could benefit of a simple subsequent separation and the broadening of the pH range of operation.

- The deposition of a carbon layer over a porous ceramic membrane and the further modification of its surface by supporting nZVI and other surface groups could bring together the advantages of oxidation reaction and simultaneous separation of both catalytic species and non-reacted compouds.

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APPENDIX

About the author

CV Resume

Selamawit Ashagre Messele was born in Addis Ababa (Ethiopia) in 1982. She obtained her B.Sc. degree in Chemical Engineering in 2005 at the Engineering Faculty of Bahir Dar University. Upon graduation, she was employed as a graduate assistant in the engineering Faculty of Bahir Dar University. She was promoted to assistant lecturer after one year work experience as a graduate assistant. In 2007 she got a European Commission Erasmus Mundus scholarship to pursuit her MSc study. In September 2009 she obtained her M.Sc. degree in Materials for Energy Storage and Conversion (MESC) from the University of Provence Aix Marseille, France, Warsaw University of Technology, Poland and University of Cordoba, Spain. In October 2009 she was awarded a four year scholarship from the Spanish Ministry of Science and Innovation to pursuit the Ph.D research at the Department of Chemical Engineering of Rovira i Virgili University. She also did a three months research stay at the Faculty of Engineering, University of Porto (FEUP), where she did surface modification of the carbon materials.

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Publications

S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Effect of activated carbon surface chemistry on the activity of ZVI/AC catalysts for Fenton-like oxidation of phenol. *Catalysis Today (In Press, DOI: 10.1016/j.cattod.2014.03.063).*

S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol. *Applied Catalysis B: Environmental 154–155 (2014) 329–338.*

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Enhanced degradation of phenol by a new Fenton-like system (Fe/EDTA/H_2O_2) at circumneutral pH. *Under review in the Journal of Water Process Engineering.*

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Catalytic wet peroxide oxidation of phenol using nanoscale zero-valent iron supported on activated carbon. *Under review in the Desalination and Water Treatment Journal.*

D. Fu, **S.A. Messele**, A. Fortuny, F. Stüber, A. Fabregat, J. Font, C. Bengoa, Efficient elimination of tyrosol in a zero valent iron-EDTA system at mild conditions. *Under review in the Chemical Engineering Journal.*

S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Zero-valent iron supported on surface modified carbon xerogel as catalysts for the oxidation of phenol by Fenton-like system. *Under preparation.*

Conference proceeding

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Phenol degradation by heterogeneous Fenton-like reaction using Fe supported over activated carbon. *Proceeding, CHISA 2012, 20th International congress of chemical and process engineering*. *Procedia Engineering 42 (2012) 1373–1377.*

Conference contributions

S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Zero-valent iron supported on surface modified activated carbon as catalysts for the oxidation of phenol by Fenton-like system. (Oral presentation), *3rd European Conference on Environmental Applications of Advanced Oxidation Processes, October 27 – 30, 2013, Almería, Spain.*

S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Nitrogen-containing activated carbon supported zero-valent iron catalyst for catalytic wet peroxide oxidation of phenol. (Poster), *3rd European Conference on Environmental Applications of Advanced Oxidation Processes, October 27 – 30, 2013, Almería, Spain.*

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Degradation of phenol by heterogeneous Fenton reaction using nanoscale zero-valent iron supported on activated carbon. (Poster), *9th European Congress of Chemical Engineering, 21–25 April 2013, The Hague, The Netherlands.*

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Heterogeneous catalytic wet peroxide oxidation of phenol using nanoscale zero-valent iron supported on activated carbon. (Poster), *7th International Conference on Environmental Catalysis, 2–6 September 2012, Lyon, France.*

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Phenol degradation by heterogeneous Fenton-like reaction using Fe supported over activated carbon. (Poster), *CHISA 2012, 20th International congress of chemical and process engineering, 25 – 29 August 2012, Prague, Czech Republic.*

I. Cota, **S.A. Messele**, A. Fortuny, F. Stüber, A. Fabregat, J. Font, C. Bengoa, Effective oxidation of azo dyes by a Fenton-type process employing zero valent iron and different chelating agents. (Poster), *CHISA 2012, 20th International congress of chemical and process engineering, 25 – 29 August 2012, Prague, Czech Republic.*

S.A. Messele, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Phenol degradation by Fenton process in presence of EDTA: Effect of pH and Fe^{2+}/EDTA ratio. (Oral presentation), *12th Mediterranean Congress of Chemical Engineering, November 15 – 18, 2011, Barcelona, Spain.*

Other contributions

S.A. Messele and J. Font, Activated carbon supported nanoscale zero-valent iron for adsorption and subsequent degradation of phenol, *10th Doctoral Day and Poster Exhibition, University of Rovira I Virgili, Tarragona, Spain, April 2013.*

S.A. Messele and J. Font, Influence of EDTA presence on phenol oxidation using the classical Fenton Process (Fe^{2+}/H_2O_2), *9th Doctoral Day and Poster Exhibition, University of Rovira I Virgili, Tarragona, Spain, April 2011.*

S.A. Messele and J. Font, Fe^{II} Carbon-supported catalysts containing immobilized chelating agents for oxidation of refractory compounds, *8th Doctoral Day and Poster Exhibition, University of Rovira I Virgili, Tarragona, Spain, April 2010.*

S.A. Messele, P.O. Villasclaras, R. Alcubilla, Fabrication and characterization of crystalline silicon solar cells for Pico satellites. (Poster*), Master thesis defense, Universite de Picardie Jules Verne, Amiens, France, September 2009.*

Research stay

January - April 2013, Faculty of Engineering, University of Porto (FEUP), Chemical Engineering Department, *Laboratory of Catalysis and Materials (LCM)*, Porto, Portugal, under the supervision of Prof. José Órfão and Dr. Salomé Soares.

Awards and recognitions

- Short stay (three months) mobility grant for European/International mentioned doctorate from the Spanish Ministry of Science and Innovation (FPI Programme, BES-2009-017016), *March 2013.*

- 1st prize of the best poster at 9th poster exhibition (500 Euros), University of Rovira i Virgili, Tarrona, Spain *(April 2011).*

- Four years doctoral scholarship from the Spanish Ministry of Science and Innovation (FPI Programme, BES-2009-017016), *2009–2013.*

- Two years European Union Erasmus Mundus Scholarship for graduate study in Materials for Energy Storage and Conversion at the four consortium universities (University of Paul Sabatier (France), University of Provence (France), Warsaw Technical University (Poland) and University of Cordoba (Spain)), *2007–2009.*

- Award for graduating with a higher grade in the undergraduate study, from Bahir Dar University on *July 7, 2005.*

- The second scholastic award as a best undergraduate student for the year *2003/04* from The Ethiopian Society of Chemical Engineers.

- The first scholastic award as a best undergraduate student for the year *2002/03* from The Ethiopian Society of Chemical Engineers.