Fenton-like oxidation of phenol with a Cu-chitosan/Al_2O_3 catalyst in a recirculating batch reactor

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1. INTRODUCTION

The freshwater available in the world continues to decrease due to the growing water demand and increasing scarcity of water sources. As a result, the recycling of industrial wastewaters is becoming an increasing need and stricter discharge standards continue to be introduced worldwide. Therefore, the efficient removal of pollutants from wastewaters arises as an important area of research.

The selection of a wastewater treatment among chemical, biological, and catalytic methods is related to the toxicities and concentrations of the pollutants in the waste stream. The pollutant´s concentrations should be high for chemical destruction methods that are thermally self-sufficient, whereas bioprocesses are suitable for nontoxic pollutants at low concentrations (Guo and Al-Dahhan 2003). Chemical treatments such as flocculation, precipitation, adsorption on activated carbon, air stripping, reverse osmosis or ion-exchange do not convert pollutants, but rather transfer them from a diluted to a concentrated stream, requiring a post-treatment (Liotta *et al.* 2009; Centi and Perathoner 2005). Thermal treatments present many drawbacks, such as severe operation conditions and considerable emission of other hazardous compounds (Liotta *et al.* 2009). Conventional biological processes represent an environmentally friendly way of treatment with reasonable costs, however, they are not adequate to treat non-biodegradable wastewaters, usually require a long residence time for microorganisms to degrade the pollutants and the disposal of sludge formed during biological treatment can pose environmental problems associated to additional costs (Liotta *et al.* 2009; Guo and Al-Dahhan 2003).

Nowadays, Advanced Oxidation Processes (AOPs) are a promising alternative, with the common trend that they generate oxygen-based radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the aqueous effluent (Gogate and Pandit 2004). Contaminants are oxidized through different reagents: ozone, hydrogen peroxide, oxygen and air or their combination. These procedures may also be combined with UV radiation (Liotta *et al.* 2009) and enhanced by catalytic materials. To choose the most appropriate technology some aspects, such as the concentration and nature of the pollutants and the volume of wastewater, must be considered (Liotta *et al.* 2009).

Among AOPs, Fenton processes (using reaction between Fe ions and hydrogen peroxide, i.e. Fenton's reagent) have emerged as a viable alternative for the wastewater treatments of medium-high total organic carbon concentrations (Liotta *et al.* 2009). Hydrogen peroxide does not form any harmful by-products, and it is a non-toxic and ecological reactant. Moreover, although hydrogen peroxide is a relatively costly reactant, the peroxide oxidation compares very favorably to processes that use gaseous oxygen. The lack of a gas/liquid boundary removes mass-transfer limitations and the hydrogen peroxide acts as a free-radical initiator, providing hydroxyl (OH•) radicals that promote the degradation of organics. This allows lowering residence times and enables conversion under milder conditions (Liotta *et al.* 2009). Furthermore, operating costs are compensated by the lower fixed capital cost with respect to ozonation and wet air oxidation (Centi *et al.* 2000).

The main reactions involved in the Fenton process are as follows (Pignatello *et al.* 2007):

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet}$
$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^{+} + HO_2^{\bullet}$
$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO^{-}$
$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$
$HO^{\bullet}$ + organics → products

The mechanism of this reagent has not been fully explained because of the variety of Fe(II) and Fe(III) complexes, numerous radical intermediate products and their consecutive reactions. A significant role is played by the formation of Fe(III) ions, which decompose H_2O_2 and produce $HO_2^{\bullet}$ radicals. The "Fenton-like" processes are characterized by the the use of Fe (II)/H_2O_2 at some step of the mechanism or iron is substituted by other active metals.

Fenton reaction has been used for the treatment of model pollutants under laboratory conditions (Barrault *et al.* 2000, Caudo *et al.* 2006, Crowther and Larachi 2003, Fathima *et al.* 2008, Inchaurrondo *et al.* 2012, Massa *et al.* 2011, Pignatello *et al.* 2007, Ramirez *et al.* 2007, Sotelo *et al.* 2004, Valkaj *et al.* 2011, Zazo *et al.* 2011) as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning etc. (Bigda *et al.* 1996, Bishop *et al.* 1968, Caudo *et al.* 2007, Dantas *et al.* 2006, Gotvajn *et al.* 2011, Hasan *et al.* 2012, Lln *et al.* 2000, Martínez *et al.* 2003, Prasad *et al.* 2007, Torrades *et al.* 2003)

One advantage of the Fenton process is that no energy input is necessary to activate hydrogen peroxide, making the reaction possible at atmospheric pressure and at room temperature. Furthermore, this method works with relatively short reaction times and uses easy-to-handle reagents (Gogate and Pandit 2003). However, the traditional Fenton reaction is strongly dependent on the presence of radical scavengers; needs a tight pH control (between 3 and 4); requires further separation of the catalyst to prevent secondary water pollution; and the complexation of the cations by reaction products such as oxalic acid or inorganic ions such as phosphate, may lead to a progressive lowering of the reaction rate and decrease of the H_2O_2 consumption efficiency (Gogate and Pandit 2003, Centi and Perathoner 2004, Fathima *et al.* 2007). For these reasons, there has been a considerable interest in the development of heterogeneous catalysts for the oxidation of wastewater streams. Recently, a great number of materials containing iron or copper as precursors supported/intercalated on/in oxides, clays, zeolite and polymers as active catalysts for Fenton-type reactions have been proposed to remove organic compounds (Castro *et al.* 2010, Chahbane *et al.* 2007, Crowther and Larachi 2003, Barrault *et al.* 2000, Bautista *et al.* 2011, Valkaj *et al.* 2007, Dantas *et al.* 2006, Garrido-Ramírez *et al.* 2010, Guibal 2005, Liou *et al.* 2005, Liou *et al.* 2009, Massa *et al.* 2011, Melero *et al* 2006).

The heterogeneous catalytic system results less sensitive to the pH and more efficient in the TOC abatement than the homogeneous one. The main difference between homogeneous and heterogeneous systems is not the formation of different active oxygen from H_2O_2, but the ability of the heterogeneous catalyst to adsorb onto its surface the phenol and/or the reaction intermediate products, favoring then their reaction with oxygen species formed by H_2O_2 activation (Caudo *et al.* 2006).

These catalysts exhibit the advantages of a heterogeneously catalyzed process and got relatively high oxidation efficiency as well as a lower sensitivity to pH compared with homogeneous catalysts at the same reaction conditions (Valkaj *et al.* 2007). Unlike the homogeneous systems, these solid catalysts could be recuperated by means of a simple separation operation and reused in next runs. However, most of them could not be used due to its lack of stability in aqueous media, due to the leaching of the active elements or/and the support.

In this context, the preparation of stable materials for heterogeneous Fenton-type processes having a good catalytic activity in a wide pH range and with negligible leaching of the transition metal, need to be addressed.

Recent studies have focused on shifting from petrochemical-based feed-stocks to biological materials to create high-performance and environmentally friendly catalysts. Polysaccharides present many advantages that may stimulate their use as polymeric supports for catalysis: 1) They are present in enormous quantity on earth, 2) they contain many functionalities that can be used readily for the anchoring of organometallic species, 3) they contain many stereogenic centers, and 4) they are chemically stable but biodegradable (Chtchigrovsky *et al*. 2009).

Among biopolymers chitin and chitosan are recommended as suitable functional materials because these natural polymers have excellent properties such as biocompatibility, biodegradability, non-toxicity, adsorption properties, etc (Viswanathana and Meenakshi 2010). Chitin is a linear chain consisting of N-acetyl-D-glucosamine (2-acetamido-2-deoxy-β-D-gluconopyranose) joined together by β(1→4) linkage. It is found in abundance in shells of exoskeletons of insects, shells of crustaceans and fungal cell wall. It is the second most common polysaccharide occurring in nature after cellulose.

Chitosan, a linear binary heteropolysaccharide, is composed of β-1,4-linked glucosamine (GlcN) with various degrees of N-acetylation of GlcN residues. Chitosan is prepared by alkaline N-deacetylation of chitin using concentrated sodium hydroxide (NaOH) solutions at high temperature for a long period of time. Chitosan is produced when the degree of deacetylation (DD) is greater than 50%. This substance is only soluble in acidic aqueous solutions and insoluble in water and alkaline solutions. When dissolved, the amino groups ($–NH_2$) of the glucosamine are protonated to $-NH_3^+$. In mildly acidic solutions chitosan can be readily cast into beads, films, and fibers, allowing for great flexibility in manipulating chitosan, and leading to unique potential as a catalyst (Macquarrie and Hardy 2005). The use of chitosan as a catalyst support agrees with some of the “green chemistry” principles such as the employment of alternative feedstocks that are more innocuous and renewable; the use of alternative reaction conditions and the design of eco-compatible chemicals (less toxic than current alternatives or inherently safer with regard to accident potential)(Centi and Perathoner 2003).

Chitosan presents diverse properties that enable its use as a catalyst support (Guibal, 2005):

(1) It is characterized by a high nitrogen content, which explains, in turn, its ability to concentrate metal ions and even neutral atoms of different metals via a variety of mechanisms such as ion exchange or chelate formation, depending on the metal and pH of the solution.

(2) Easy modification and even possibility to use it without preliminary modification.

(3) High metal dispersion on the surface of a chitosan support.

(4) Rather high thermal stability, durability.

(5) Easy recovery of valuable components from the catalysts by incineration and metal extraction.

However, pure chitosan has some disadvantages such as unsatisfactory mechanical properties, severe shrinkage, deformation after drying, solubility under acidic conditions, and compressibility at high operating pressure. Several methods to overcome these disadvantages have been performed by coating or impregnating chitosan on rigid porous materials. Coating chitosan as a thin layer onto an immobilization support increases the accessibility of its binding sites, improves the mechanical stability and reduces the amount of chitosan needed (Futalan et al. 2011, Ngah *et al.* 2011, Tsvetkova *et al.* 2007, Wan *et al.* 2005).

Chitosan has been immobilized in different supports such as bentonite, montmorillonite, perlite, alumina, etc., and used as an adsorbent for several purposes like the removal of heavy metals (Boddu *et al.* 2008, Chang *et al.* 2006, Dalida *et al.* 2011, Gandhi *et al.* 2010, Hasan *et al.* 2008, Popuri *et al.* 2009) or dyes (Lee *et al.* 2009, Ngah *et al.* 2010, Wang and Wang 2007, Zhu *et al.* 2010). Moreover, chitosan has been use as a catalyst support for a variety of reactions: oxidation of catechol to n-quinone (Yang and Vigee 1991); reduction of 4-nitrophenol (Wei *et al.* 2010); cyclopropanation of olefins (Wang *et al.* 2003); chemical fixation of carbon dioxide to cyclic carbonate (Xiao *et al.* 2005); asymmetric hydrogenation of ketones (Wei *et al.* 2004); oxidation of catecholamines (Chiessi and Pispisa 1994); aldol and Knoevenagel reactions (Kuhbeck *et al.* 2011); nitroaniline degradation (Vincent 2004); allylic substitution reactions (Beadoux *et al.* 2007); reduction of methylene blue (Rezende *et al.* 2010); carbonylation to esters of Naproxen (Zhang *et al.* 2003); hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol (Wu *et al.* 2007); hydrogenation for nitrobenzene (Huang *et al.* 2001); reduction of chromate (Vincent and Guibal 2002); Suzuki and Heck reactions (Ardí *et al.* 2003); synthesis of Jasminaldehyde (Sudheesh *et al.* 2010); Huisgen Cycloaddition (Chtchigrovsky *et al.* 2009); hydrolysis of phosphodiester (Chan and Cheng, 2009).

However, only few publications employed chitosan as a catalyst support for Fenton reactions. Castro *et al.* (2009) studied different supported Cu(II) polymer catalysts (PVP2, PVP25, or chitosan beads) for the catalytic oxidation of phenol at 30º C, at atmospheric pressure using air or H_2O_2 as oxidants. Sulakova *et al.* (2007) prepared Cu(II)/chitosan complexes for degradation of five model azo textile dyes in aqueous solution with hydrogen peroxide. Kucherov *et al.* (2003) prepared series of heterogenized copper complexes by either coprecipitation or adsorption of Cu(II) on the bulk chitosan and composite supports (egg-shell type chitosan/SiO2 and chitosan/MCM-41systems).

Chensi Shen *et al* (2010) prepared a CoTSPc@chitosan catalyst, by immobilizing covalently water soluble cobalt (II) tetra-sulfophthalocyanine onto adsorbent chitosan microspheres. The catalyst was tested in the oxidation of C. I. Acid Red 73 with H_2O_2. Zubieta *et al.* (2008) evaluated the remotion (adsorption plus degradation) of two reactive dyes, Methylene Blue (MB) and Benzopurpurin (BP), from aqueous solutions by the utilization of TiO_2-chitosan microporous materials. Lee *et al.* (2010) investigated the degradation of trichloroethylene (TCE) by a modified Fenton reaction in aqueous solution, at neutral pH, with a catalyst of Fe(II) chelated by cross-linked chitosan.

The objective of the present study is to synthesize and characterize a new Cu/chitosan composite catalyst obtained by immobilizing Cu-chitosan complexes onto γ-alumina and study its performance in the Catalytic Wet Peroxide Oxidation (CWPO) of phenol in a fixed bed recirculating reactor, at atmospheric pressure and moderate temperature of 50°C. The term catalyst immobilization or heterogeneization can be defined as “the transformation of a soluble catalyst into a heterogeneous one, which is able to be separated from the reaction mixture and preferably be reused for multiple times”. Several methods have been employed for linking metal complexes to solids supports, either onto external surface or into the interior pores such as formation of covalent bonds or noncovalent interactions (physisorption, electrostatic interactions, H-bonding). Following green chemistry principles, physisorption was the method selected in this contribution.

2. EXPERIMENTAL

2.1. Catalyst preparation and characterization

The Al_2O_3/chitosan-Cu(II) catalyst was prepared by coprecipitation of the Cu-chitosan complex onto alumina spheres. The Cu-chitosan complex was obtained by dissolving 1.5 g of chitosan (medium molecular weight chitosan, 75–85% deacetylation, from Sigma–Aldrich) and 8.05 g of $CuCl_2 \cdot 2H_2O$ in 300 ml of HCl (0.1 mol/L). The mixture was stirred until the formation of a blue clear solution.

Prior to the impregnation procedure, the γ-alumina (provided by Sasol, median particle diameter of 1.76 mm and total pore volume of 0.78 mL/g.) was washed several times with distilled water. The sample was dried for 24 h at 323 K, it was then added into the chitosan-Cu^{2+} solution in an Erlenmeyer of 250 mL and stirred for 30 min.

The solid was filtered and rinsed with distilled water several times before being contacted with a 0.1 mol/L NaOH solution for about 15 min, which neutralised the HCl within the chitosan gel and thereby coagulated and deposited the Cu-chitosan complex on the alumina surface. The sample was filtered and washed again with distilled water until the filtrate was neutral, in order to remove any NaOH. The particles obtained were dried at room temperature for 48 h and then at 323 K for 24 hours.

The copper content of the catalyst was determined by soaking the sample in 65% HNO_3 solution and then analyzing the copper concentration using Atomic Absorption Spectroscopy (AAS) in an ANALYST 300 Perkin-Elmer

Spectrophotometer. Copper leached from the catalyst during oxidation tests was also measured by AAS.

The specific surface area (BET) was measured with a Micromeritics ASAP 2000 instrument using N_2 adsorption at 77 K.

Thermogravimetric analysis (TGA) was performed to confirm the existence of the complex Cu-Chitosan onto the γ-alumina. Samples of 18 mg approximately were taken for this purpose. Data were captured using a TGA (Shimadsu, model TGA-50) instrument with a constant airflow of 20 mL/min. The heating rate applied was 10ºC/min and the temperature was increased from 25ºC to 800 ºC. However, the temperature was first kept constant at 110ºC for 30 min in order to assure the complete removal of water contained in the sample. Table 2.1 presents results from the catalyst characterization.

Table 2.1. Catalyst characterization

Copper content (%)	1.2
BET Area (m^2/g)	167
Chitosan content (% wt)	2.44
Particle diameter (mm)	1.76

2.2. Fenton like oxidation of phenol aqueous solutions

2.2.1. Reaction Set-up

The CWPO was performed in a fixed bed recirculating reactor packed with the home–made Cu-chitosan/Al_2O_3 catalyst. This set-up presents some advantages over the continuous reactor. It is a smaller device that uses small amounts of catalyst and reactants and, although the one-pass conversion is lower (differential reactor), much higher conversions can be achieved through prolonged exposure to the catalyst within the fixed bed. Additionally, as one-pass conversion does not require to be large, there is no need of a significant liquid residence time in the reactor and this allows extension of the examined liquid velocity range, using a reasonable amount of catalyst; consequently, conditions attained at high and low velocities can be studied without changing the set-up. An image of the reactor is shown in Figure 2.1.

Figure 2.1. Set up of the trickle bed reactor used in this study

A load of 41 g of the Cu(II)-chitosan/alumina catalyst was used in the CWPO of a phenol solution of 1 g/L (Panreac, 99 %) in a recirculating jacketed packed bed glass reactor (60 cm long and 2.35 cm of internal diameter) operated at 323 K and 1 atm in cocurrent downwards operation. In this reactor the ratio load of catalyst to load of liquid is high and this enables a rapid mineralization of the intermediates generated during phenol oxidation, which helps preserving the catalyst stability. Also it allows minimizing the contribution of secundary homogeneous reactions and this higher concentration of active sites may have a beneficial effect on oxidation performance due to the increasing amount of active sites for H_2O_2 decomposition and for organic compounds adsorption (Ramírez *et al.* 2007). The increase of copper sites should induce a better use of oxidant for the promotion of free radicals, avoiding its thermal decomposition into O_2 and water (Sotelo *et al.* 2004)

Air was introduced at the top of the reactor at a flow rate of 50 mL/min. The liquid feed consisted of 600 mL of a phenol solution, which was kept in a flask inside a thermostatic bath, and recirculated at a flow rate of 45 mL/min through the column. A dose of 11.65 mL of H_2O_2 (30% wt) was added into the phenol solution flask to initiate the reaction. Once it was consumed, a second dose of 11.65 mL was added. The total amount of added oxidant was 2.57 times the stoichiometric requirement.

Five tests of 4 hours each, at identical conditions, were performed, using the same load of catalyst but a fresh phenol solution each time. Catalyst leaching was evaluated over a total period of 20 hours. Phenol, TOC and H_2O_2 concentrations and pH values were measured along the reaction time.

2.2.2 Analytical methods

During CWPO tests, liquid samples were taken at different time intervals and immediately analyzed. Phenol was detected and measured by a standard colorimetric method (Clesceri and Greenberg 1998). Hydrogen peroxide was detected by an iodometric titration method (Clesceri and Greenberg 1998).

Total Organic Carbon (TOC) values were obtained by a TOC Analyser (Analytic Jena, model NC 2100). Samples were acidified with 50 ml HCl 2 mol/L, then were bubbled with synthetic air for 3 min to eliminate the inorganic carbon content and finally injected.

Phenol, TOC and H_2O_2 conversions were evaluated at different times up to 240 min. Data shown here represent an average of at least three experiments, which showed satisfactory repeatability.

Identification of intermediates was carried out in a HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS). The analyses were performed using a mobile phase with a gradient mixture of methanol and ultra pure water (Milli-Q water, Millipore) from 0/100 v/v to 40/60 v/v. The flow rate increased from 0.6 at the fifth minute to 1.0 mL/min at the seventh minute. The pH of the water was previously adjusted at 1.41 with sulfuric acid. A diode array detector was used for detecting the organic compounds analysed at 254 nm or 210 nm, depending on the compound to be identified.

3. RESULTS AND DISCUSSION

3.1. Blank experiment

A preliminary blank experiment to discriminate the effect of adsorption was performed with the Al_2O_3 support and in absence of oxidant. In the absence of copper, phenol removal took place essentially by adsorption, with maigre phenol and TOC conversions of around 17%.

3.2. Activity and Stability tests

The catalyst was used in five tests of 4 hours each, under the same conditions, using a fresh phenol solution each time.

During the first test, a TOC conversion of 90% was obtained. Phenol and H_2O_2 were completely consumed. The H_2O_2 was rapidly decomposed into radicals that allowed a fast mineralization of the carboxylic acids generated during the oxidation of phenol.

Phenol and TOC conversions against time are presented in Figure 3.1 (A) and H_2O_2 concentration and pH evolution in Figure 3.1 (B).

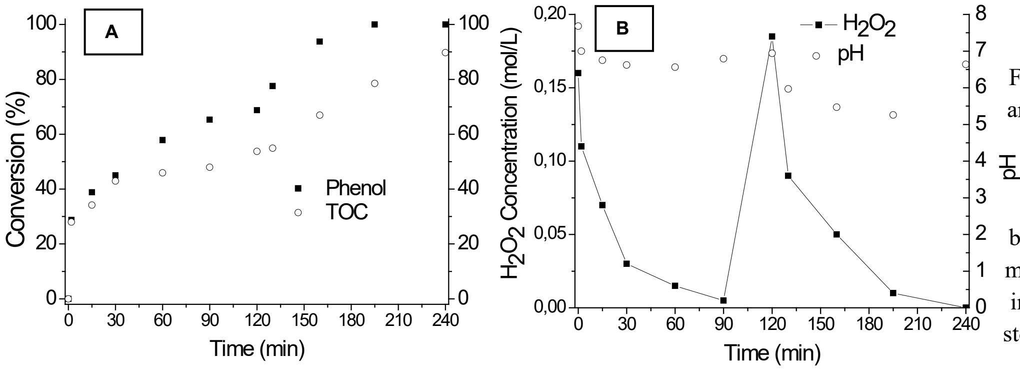

Figure 3.1. Evolution of phenol and TOC conversions (A) and pH and H_2O_2 concentration (B) over time. 600 ml of 1 g/L phenol; 41 g of 1% Cu catalyst bed; phenol solution flow: 45 mL/min; temperature: 323 K; initial dose of H_2O_2: 1.3 times the stoichiometric value.

The HPLC identification of intermediates indicated the presence of a low concentration of aromatics (hydroquinone, catechol, p-benzoquinone), which were finally oxidized into biodegradable carboxylic acids (mostly succinic, maleic, malonic and oxalic acids). The distribution of intermediates is presented in Figure 3.2 and the percentage of phenol, identified and unidentified compounds are shown in Figure 3.3.

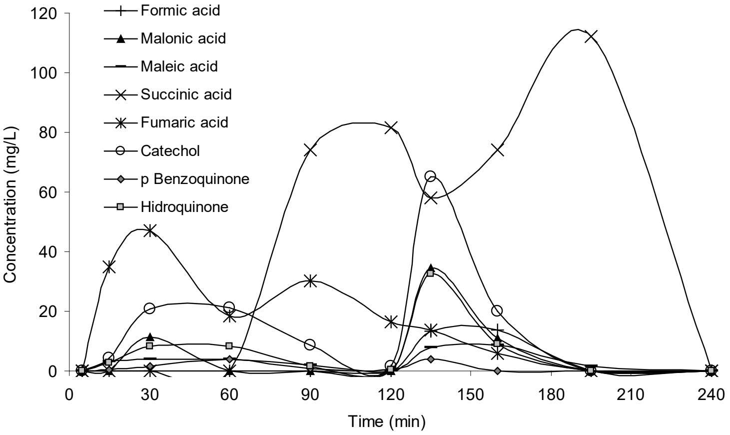

Figure 3.2. Intermediates distribution against time, first test, 600 ml of 1 g/L phenol; 41 g of 1% Cu catalyst bed; phenol solution flow: 180 mL/min; temperature: 323 K; initial dose of H_2O_2: 1.3 times the stoichiometric value.

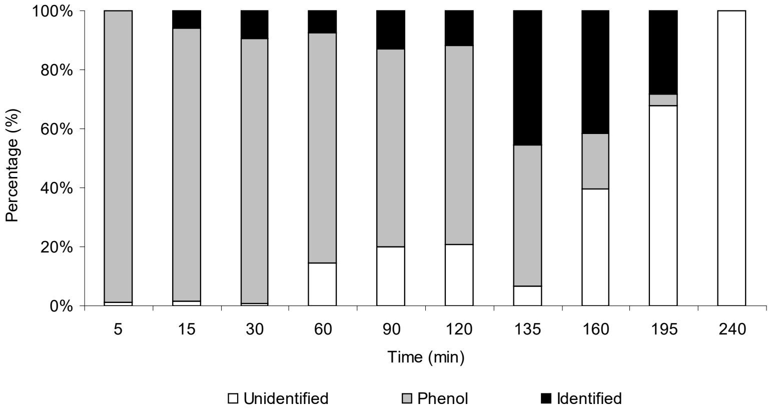

Figure 3.3. Percentage of phenol, identified and unidentified products in the intermediates distribution against reaction time, during the first test.

Initially, phenol is converted to hydroquinone and catechol. As catechol is the main primary oxidation product, hydroxylation seems to take place predominantly in the ortho position. Next, these compounds are oxidized to o- and p-benzoquinone. These colored intermediates are much more toxic than phenol and thus their presence even at low concentration would mean high values of ecotoxicity (Zazo *et al.* 2005, Suárez-Ojeda *et al.* 2007). Then, ring-opening of the aromatic intermediates leads to the formation of organic acids. Fumaric, maleic, malonic, succinic and oxalic acids were the identified products at this stage. During the experiment, the color of the reaction system turned from transparent to light pink due to the presence of p-benzoquinone and became again clear as the reaction progressed.

As it is shown in Figure 3.3 in this HPLC preliminary analysis was not feasible to identify a high percentage of reaction intermediates (possibly dimmers and high condensation products), a situation commonly encountered by other researchers (Zazo *et al.* 2005, Zazo *et al.* 2009, Villota *et al.* 2007).

The high degree of mineralization and low accumulation of acids was proved by the pH evolution, which stayed above 6 during most of the reaction, with a minimum of 5.3. Nevertheless, it was suspected that some carboxylic acids were absorbed by the catalyst. During the first four hours of use, no copper was detected in the liquid phase; therefore metal leaching was negligible.

Catalyst stability was addressed using the same load in four identical consecutive runs of four hours each. Catalyst was not pretreated between tests. In each experiment, the equipment was loaded with fresh phenol and hydrogen peroxide solutions. Runs were performed at identical operating conditions, except that, due to accumulation of carboxylic acids, the initial pH values were progressively lower (up to 5.5). Furthermore, the pH evolutions also presented lower pH values and leaching of the catalyst was observed, as seen in Figure 3.4.

The final TOC and phenol conversions and the residual H_2O_2 concentration at the end of each test are presented in Figure 3.5.

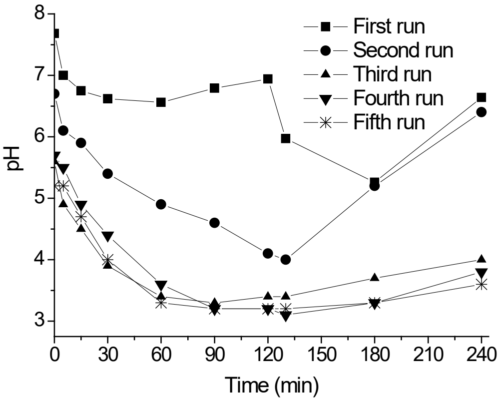

Figure 3.4. pH evolution against time for each test. 600 ml of 1 g/L phenol; 41 g of 1% Cu catalyst bed; phenol solution flowrate: 45 mL/min; temperature: 323 K; initial dose of H_2O_2: 1.3 times the stoichiometric value.

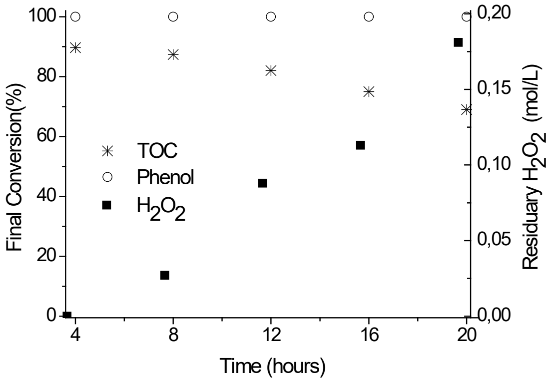

Figure 3.5. Final TOC and phenol conversions and residual peroxide concentrations at the end of each run. 600 ml of 1 g/L phenol; 41 g of 1% Cu catalyst bed; phenol solution flowrate: 45 mL/min; temperature: 323 K; initial dose of H_2O_2: 1.3 times the stoichiometric value.

During the following runs, complete phenol conversion was obtained at the end of each reaction. However, the H_2O_2 decomposition and final TOC conversion decrease with use. The final concentration of oxidant increases due to a lower rate of radical generation, which causes the TOC conversion to drop. As a result, the final TOC conversion decreased from an 89.7 % in the first test up to a 69 % after 20 hours of usage (20% reduction).

Variations in the effluent colour and pH evolution evidenced a different product distribution. The colour of the supernatant at the end of the following reactions turn brown due to the presence of benzoquinones and the pH reached lower values due to a higher accumulation of carboxylic acids. As an example, colour evolution of the reaction media with a catalyst used 16 hours is presented in Figure 3.6. Furthermore, catalyst colour changed from light blue to light brown as time elapses, due to the presence of adsorbed intermediates.

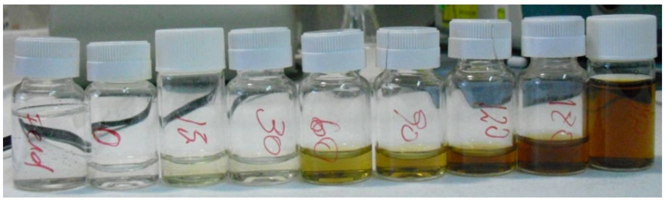

Figure 3.6. Colour evolution of the reaction media in the fifth test.

The amount of copper leached from the catalyst at the end of each reaction and present in the liquid phase was evaluated by AA experiments. Results (as %leaching and ppm) are presented Figure 3.7. Taking into account these measurements, it was possible to evaluate the copper content of the catalyst at any time, substracting the total leached copper from the initial load. Using this approach, the copper load decreased from 1.2% to 1% after 20 hours of usage.

The homogeneous contribution should not be significant compared to the heterogeneous phenomena, as the catalyst load employed in this experiment is quite high. This is evidenced by the first run, where no leaching takes place and the final conversions are the most significant. Moreover, the copper leached can be directly sequestered by organic acids and diacids forming copper species often having lower activity (Caudo *et al.* 2007).

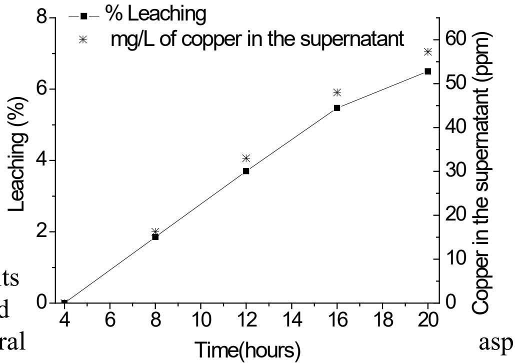

Figure 3.7. Copper leached from the catalyst at the end of each reaction.

The results presented in Figures 3.5 and 3.7 are a clear signal of reduced performance, which becomes more evident after 8 h of use. Several aspects could contribute to the observed results: metal leaching, adsorption of intermediate products and lower initial pH conditions (these three factors directly affect catalyst activity) and even poor liquid distribution (leading to decreasing catalyst utilization due to localized catalyst deactivation). Therefore, additional experiments were carried out to independently assess the contribution of each aspect on the overall performance.

3.3. Deactivation Phenomena

To discriminate the effects of leaching, adsorption of intermediate products and initial pH, on catalyst performance, additional tests were performed in a slurry reactor, in which wetting is complete.

3.3.1. Effect of Intermediate Products Adsorption

To evaluate the effect of adsorption of intermediates, phenol oxidation tests were done comparing the performance of used and fresh catalyst with the same initial amount of metal present, at identical initial pH conditions and with complete wetting (slurry reactor). Experiments were carried out in a 250 mL stoppered glass reactor equipped with a condenser, thermocouple and a pH electrode, provided with vigorous agitation and in contact with air at atmospheric pressure. Tests were performed at 50°C for 1 hour. Amounts of 0.50 g of used and 0.42 g of fresh catalyst were employed, which is equivalent to 29.4 mg/L of copper in the solution, therefore experiments were performed using the same initial load of copper. Catalysts were contacted with 170 mL of 0.1 g/L of phenol aqueous solution under continuous stirring. An excess of hydrogen peroxide was added to the system (190 mmol/L or 1.3 the stoichiometric requirement) and the reaction started.

The TOC and phenol conversions achieved at 60 min are presented in Table 3.1.

Table 3.1 Comparison of fresh and used catalyst performances

Catalyst sample	TOC Conversion (%)	Phenol Conversion (%)
Fresh	56	100
Used	57	100

According to these results, the adsorption of intermediates has no effect on TOC and phenol conversions.

3.3.2. Initial pH effect

Tests were performed in the slurry reactor using 2 g of fresh catalyst, at 50°C, with 170 mL of 1 g/L phenol solution and a hydrogen peroxide initial concentration of 190 mmol/L (1.3 the stoichiometric requirement). The first test was carried out at pH = 7, a value close to the usual initial pH of the phenol solution. The second test was performed with an initial pH of 5, adjusted by adding a few drops of HCl. The final TOC, phenol and H_2O_2 conversions achieved at 240 min are presented in Table 3.2.

Table 3.2. Effect of initial pH on reaction outcomes (fresh catalyst)

Initial pH	TOC Conversion (%)	Phenol Conversion (%)	H_2O_2 Conversion (%)
5	75,5	100	79
7	74	100	75

According to these results, the initial pH has little effect on the reaction evolution, at least in this pH range.

3.3.3. Copper load effect

As it was found that the initial pH and adsorbed intermediates have no significant effect on the final TOC conversion, the effect of copper load was analyzed in experiments performed in the slurry reactor using different amounts of fresh catalyst, at 50°C, with 170 mL of 1 g/L phenol solution, a hydrogen peroxide initial concentration of 190 mmol/L (1.3 the stoichiometric requirement) and initial pH=7. Results are presented in Table 3.3.

Table 3.3. Effect of catalyst load on reaction outcomes

Copper Load (g/L)	TOC Conversion (%)	Phenol Conversion (%)	H_2O_2 Conversion (%)
19.3	89.5	100	96
9.7	75.8	98	82
4.8	60	96	66

Results in Table 3.3 indicate that increasing the copper content by a factor of almost 4 (while the other conditions remain constant) renders an enhancement of TOC conversion of 30%. Accordingly, it is uncertain to strictly attribute the 20% TOC reduction depicted in Figure 3.4 (from 89.7 to 69%) to the 20% loss of copper measured.

However, the liquid-catalyst contact (or wetting efficiency, f) may not be complete along the reactor, leading to some unused catalyst fraction (f= 0.55) (Baussaron *et al* 2007). Therefore the leaching effect could be more significant in the fraction of the trickle bed that is actually used (wetted fraction) during the reaction.

3.3.4. Liquid flow rate effect

The effect of wetting on performance was explored. A test after the fifth run was carried out using a phenol flowrate of 180 mL/min (f = 0.8). A TOC conversion of 83.5% was obtained after 240 min. In spite of the lower copper content of the used catalyst, the adsorbed intermediate products and the lower initial pH, the TOC conversion attained at a higher liquid flowrate was 20% larger than that obtained at the end of the fifth run (69%), but using a small liquid flowrate.

Additional experiments were performed in order to specifically assess the effect of phenol flowrate. The tests were carried out in the fixed bed recirculating reactor packed with identical catalyst loads previously used during 4 hours. Two different phenol flowrates were investigated: 45 and 180 mL/min. Figure 3.8 and 3.9 presents repectively phenol and TOC conversions against time, for both liquid flow rates. Figure 3.10 presents the H_2O_2 concentration (A) and pH (B) evolution for each flow.

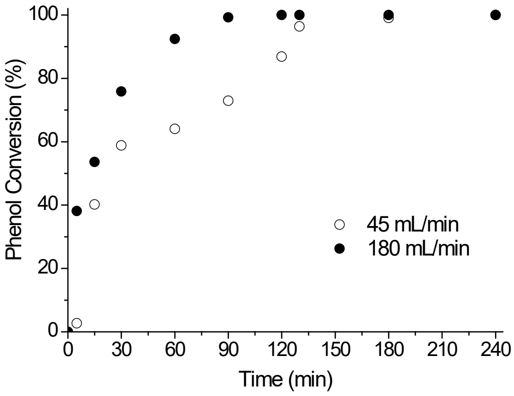

Figure 3.8. Phenol conversion evolution against time for each phenol flow rate (45 mL/min and 180 mL/min).

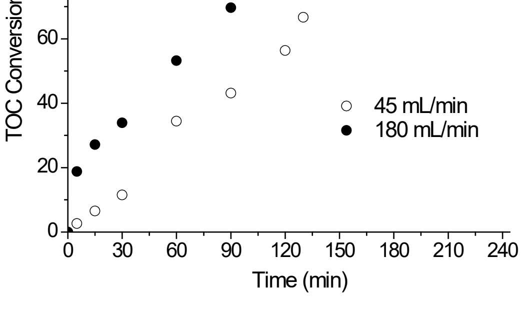

Figure 3.9. TOC conversion evolution against time for each phenol flow rate (45 mL/min and 180 mL/min).

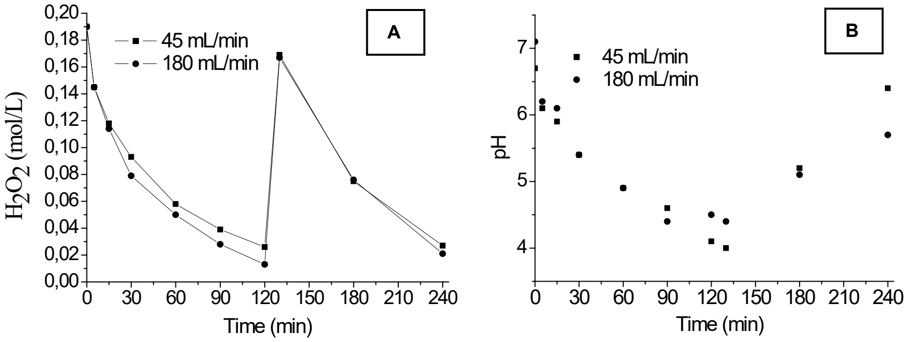

Figure 3.10. H_2O_2 concentration (A) and pH (B) evolution against time for each phenol flow rate (45 mL/min and 180 mL/min).

With a flowrate of 180 mL/min, the initial phenol, H_2O_2 and TOC conversion rates resulted higher than those achieved with the lower flow rate. Phenol was completely oxidized in approximately 100 min and a TOC reduction of 80 % was obtained in 120 min with a final conversion of 90% at the end of the reaction. When the flow rate is increased, the hydrodynamic conditions are modified and the contact between the liquid and the catalyst or wetting efficiency is improved from 0.55 to 0.8 approximately. This favors the generation of radicals and also the termination reactions over the catalyst surface.

Just like in the previous tests, and additional H_2O_2 dose of 11.65 mL was added at 120 min. This extra oxidant amount has nil impact on the high phenol and TOC conversions, achieved at the highest liquid flowrate but increases phenol and TOC conversions obtained working with a 45 mL/min flowrate. For both experiments, the additional oxidant dose increases pH values due to the mineralization of carboxylic acids. The measured leaching of copper was the same under these different conditions. In both test the leaching resulted less than 2%.

CONCLUSIONS

The home-made Cu-quitosan/alumina catalyst successfully oxidizes a phenol solution of 1 g/L in a laboratory recirculating packed bed glass reactor operated at 323 K and 1 atm, employing gas and liquid flowrates of 50 and 45 mL/min respectively in cocurrent downwards operation. Complete phenol and H_2O_2 consumption and a TOC conversion of 90% were obtained after two hours with a small excess of H_2O_2. No metal leaching was detected.

Catalyst stability was addressed using the same load in four identical consecutive runs of four hours each, during 20 hours. A complete phenol conversion was maintained but the TOC conversion decreased from 89.5% in the first run to 69% at the end of the last test. A final copper leaching of 20% was estimated. In spite of this loss, the system still maintained a high copper load; therefore it was uncertain to attribute the deactivation only to the leaching of the active metal. The adsorption of intermediate products and drop of the initial pH were proven not to be related to the deactivation process. However, the uncomplete liquid-catalyst contact lead to some fraction of unused catalyst, which accentuated the leaching effect in the fraction of the trickle bed that was actually used. This was proven by increasing the phenol flowrate from 45 mL/min to 180 mL/min, in a test performed with a load of catalysts used during 20 h. The increase of the liquid flowrate favoured the effective wetting of the catalyst, promoting the generation of more radicals and also the termination reactions over the catalyst surface. Consequently, the final TOC conversion achieved at better wetting conditions (89%) was significantly higher than the value obtained in the previous test (69%), with a lower flow rate.

The effect the phenol flowrate was further studied. With a higher flow rate, the initial phenol, TOC and H_2O_2 rates increased in comparison with results obtained at the lower flow rate. With the highest flowrate, complete conversion of phenol and 80% conversion of TOC were achieved, in only 120 min, before adding the second dose of oxidant. According to these results, under these conditions, it is possible to obtain a higher mineralization with a lower amount of oxidant by increasing the phenol flow rate.

The catalyst proved to be active for phenol mineralization, showing a 90% of TOC conversion at the end of the reaction. However, some copper leaching was detected which could be removed by precipitation, membrane filtration or adsorption before feeding the effluent into a subsequent treatment.

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