

## Synthesis of copper catalysts by coprecipitation of Cu(II) and Chitosan onto Alumina

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### Abstract

Three Cu-Chitosan composite catalysts were prepared by coprecipitation of a Cu-Chitosan complex onto cylindrical pellets in subsequent impregnation steps. Samples were used in the wet peroxide oxidation (WPO) of phenol solutions at 30°C and 1 atm. All catalysts were active for phenol degradation, showing up to 100% of phenol conversions. Leaching of the active species during reaction was detected.

Keywords: coprecipitation, copper, alumina, chitosan, catalytic oxidation

### 1. Introduction

The use of heterogeneous systems for CWPO has received considerable attention in the last years. Transition metal complexes supported on diverse surfaces were investigated as potentially active catalysts in a variety of reaction systems.

More stringent environmental regulations require the development of technological systems for the removal of organic pollutants that are difficult to degrade by conventional chemical and/or biological methods. Recent investigations revealed that most compounds found in waste water could be oxidized by advanced oxidation processes (AOPs). Usually, AOPs are carried out at near ambient conditions and combine treatments with UV-light and H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> or TiO<sub>2</sub> (Sykora et al., 1997). Hydrogen peroxide is a moderate oxidizing agent but, when used in combination with a catalyst, UV-light, ultrasound or light, it can successfully degrade most organic compounds (Caudo et al., 2006). In these systems, H<sub>2</sub>O<sub>2</sub> decomposes with the formation of free radical intermediates (OH●), that can react with a variety of organic compounds allowing partial or complete degradation.

The utilization of heterogeneous catalytic systems for AOPs has received considerable attention in the last years. Transition metal complexes supported on

diverse surfaces were used as potentially active catalysts and tested in a variety of reaction systems (Pestunova, et al., 2003). Particularly, a growing number of studies reporting on Chitosan as a catalytic support have been published over the last two decades (Guibal, 2005). This biodegradable polysaccharide is one of the most abundant natural polymers and exhibits a remarkable capability to adsorb metal ions. Chitosan is obtained from chitin (a material found in crab or shrimp shells) by deacetylation. Chitosan-supported catalysts were used in several processes (Guibal et al., 2005). Sulakova et al., (2007) studied the degradation of five model azo textile soluble dyes with hydrogen peroxide in the presence of Cu(II)-Chitosan globules. The rate of decolorization was found to be depended on pH, Cu(II) concentration, dye and hydrogen peroxide concentrations. Catalyst stability also depended on pH and H<sub>2</sub>O<sub>2</sub> concentration.

For most of the studies presented in the literature (Weng at al., 2007) Chitosan has been used in the form of flakes, powder or hydrogel beads. Under reaction conditions, it has the tendency to agglomerate, to form gel or even to dissolve in the aqueous medium. To overcome this problem, SiO<sub>2</sub>-Chitosan composites have been developed (Kucherov et al, 2003).

In this context, the aim of this work is to both synthesize and characterize new Cu-Chitosan composite catalysts obtained by coating Cu-Chitosan complexes onto  $\gamma$ -alumina in consecutive impregnation steps. Then the catalysts were used for the WPO of phenol in a laboratory batch reactor.

## 2. Materials and methods

### 2.1. Materials

Hydrochloric acid fuming was obtained from Merck (Ref. 21529), Chitosan at medium molecular weight was purchased from Sigma-Aldrich (Ref. 448877), Dihydrated copper chloride was obtained from Cicarelli laboratories (Ref. 902211) and  $\gamma$ -alumina was provided by Sasol (Ref. 604130) with an average of 3 mm of diameter and 3 mm of height . The catalytic activity was evaluated by performing the oxidation of phenol, a model compound, using hydrogen peroxide as oxidant. Phenol was purchased from J.T. Baker (Ref. 2858-01) and Hydrogen peroxide (30%V) was obtained from Cicarelli laboratories (Ref. 805110).

### 2.2. Catalyst preparation

The catalysts were synthesized by impregnation of the Cu-Chitosan complex onto  $\gamma$ -alumina. In each impregnation step, the Cu-Chitosan complex was prepared by dissolving 2g of Chitosan and 4g of Cu(II) ions into 300 ml of HCl (0,1M). Then, 40 g of  $\gamma$ -alumina (previously washed with distilled water) was put in contact with the Cu-Chitosan complex. After 15 min, the liquid was drained and the excess of superficial copper complexes or copper ions were removed by washing with distilled water. The catalyst was dried at room temperature in air. The drying process was completed in a stove at 100°C during 30 min. The impregnation steps were repeated, following the same experimental protocol, and therefore three catalysts were prepared: P1, P2 and P3, in which  $\gamma$ -alumina pellets were exposed to one, two or three impregnation cycles.

### 2.3. Catalytic oxidation

The oxidation tests were conducted at 30°C and 1 atm in a laboratory batch stirred reactor of 180 ml. The initial phenol concentration was always 1 g·L<sup>-1</sup>. The amount of catalysts P1, P2 and P3 was 3g. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used at the stoichiometric Phenol:H<sub>2</sub>O<sub>2</sub> molar ratio of 1:14. Reaction progress was periodically monitored by withdrawing 2 mL of liquid from the reaction medium every 20 minutes. Then, 1 mL sample was analyzed by HPLC to determine the remaining concentration of phenol and H<sub>2</sub>O<sub>2</sub> and 1 mL sample was analyzed by TOC analyzer.

### 2.4. Analytical procedure

The thermogravimetric analysis (TGA) were performed to confirm the existence of the complex Cu-Chitosan onto the  $\gamma$ -alumina, and also to characterize the catalyst of Cu(II)-Chitosan-alumina. TGA data was obtained using a TGA (Shimadzu, model TGA-50) instrument. Samples of 18 mg approximately were taken for this purpose. It was used a constant airflow of 20 mL·min<sup>-1</sup>. The heating speed applied was 10°C·min<sup>-1</sup> and the temperature was increased from 25°C to 800 °C. The temperature was kept constant at 110° during 30 min in order to assure the complete removal of water contained in the sample.

The catalysts samples were also evaluated by using a Temperature-Programmed Reduction analyzer (TPR). This method was applied to identify reducible species onto the  $\gamma$ -alumina after the coprecipitation process. Samples of 20 mg of catalyst were used. The TPR runs were performed using 5% H<sub>2</sub>/Ar (vol.) mixture to reduce the samples. The gas flow was 20 cm<sup>3</sup>·min<sup>-1</sup> and the heating rate was 7°C·min<sup>-1</sup> between the temperature range of room temperature and 500°C.

The copper content of the catalyst was calculated by using Atomic Absorption Spectrometer (Perkin Elmer, model 3110). Samples were diluted in order to avoid a saturated signs at copper concentrations more than 5 mg·L<sup>-1</sup>. The analyses were performed at 325 nm with a specific lamp for the element of Cu (Perkin Elmer, serial number 01074), which worked with continuous current at 15 mA.

Phenol conversion was calculated by measuring the phenol concentration by 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 increases from 0,6 to 1,0 mL·min<sup>-1</sup>. The pH of the water was adjusted at 1,41 with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The detection was performed by UV absorbance at a wavelength of 254 nm. Automatic injector analyzed volumes of 20  $\mu$ L per sample. A calibration curve of phenol was made using aqueous samples of known composition. Intermediates identification was performed by HPLC analyzer using aqueous samples of known patterns of each intermediate.

TOC was analyzed by a Total Organic Carbon Analyzer (Analytic Jena, model NC 2100). Samples were acidified with 50 mL HCl 2N then were bubbled with synthetic air for 3 minutes to eliminate the inorganic carbon content and then injected.

### 3. Results and discussion

#### 3.1. Copper content

The amount of copper present in each catalyst was measured by Atomic Absorption. Results for fresh samples are reported in Table 1. As observed, when the number of impregnation steps was increased, the amount of copper present in the samples also increased, but the difference between two and three impregnation steps was not significant (4,7%)

Table 1. Cu content of fresh catalysts

Sample	Cu content(mg·g <sup>-1</sup> )
P1	20.4
P2	31.8
P3	33.3

#### 3.2. Wet Peroxide Oxidation

Figure 1 presents phenol conversions against time for the three catalysts tested. Operating conditions are stated in the figure caption. It can be observed that all the samples were able to oxidize phenol at ambient conditions. Initial reaction rates were higher for catalysts P2 and P3, which contained approximately the same amount of copper, as indicated in Table 1.

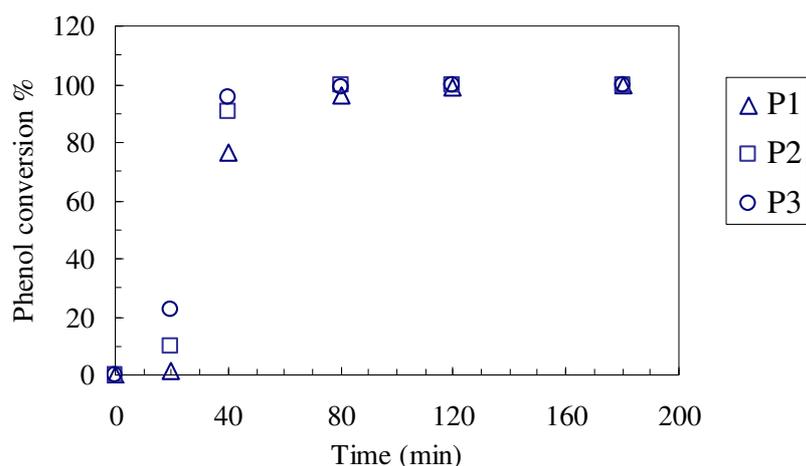


Figure 1. Phenol conversion vs time.  $[Ph]_0 = 1 \text{ g}\cdot\text{L}^{-1}$ , Phenol:H<sub>2</sub>O<sub>2</sub> molar ratio = 1:14, T=30°C. Reaction time = 3h.

Figure 2 presents the TOC profiles obtained for the three samples during reaction. TOC values increased with time for all the catalysts, but samples P2 and P3 presented better performances.

Additionally, total mineralisation was not achieved for any sample, so the presence of intermediates products after three hours of reaction can not be neglected.

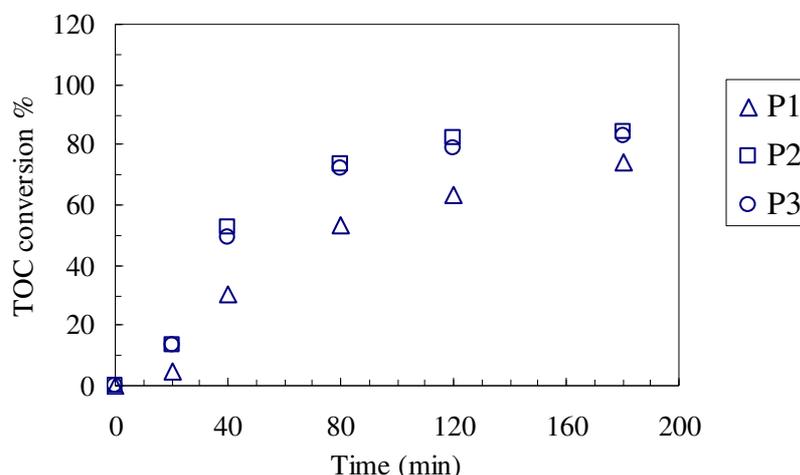


Figure 2. TOC conversion vs time:  $[\text{Ph}]_0 = 1\text{g}\cdot\text{L}^{-1}$ , Phenol: $\text{H}_2\text{O}_2$  molar ratio = 1:14,  $T=30^\circ\text{C}$ . Reaction time = 3h.

Figure 3 represents pH evolution with time. As observed for the three catalysts, pH values decrease as reaction time increases, indicating the presence of refractory acidic intermediates, responsible for the differences observed between values of phenol conversion represented in Figure 1 and TOC data showed in Figure 3.

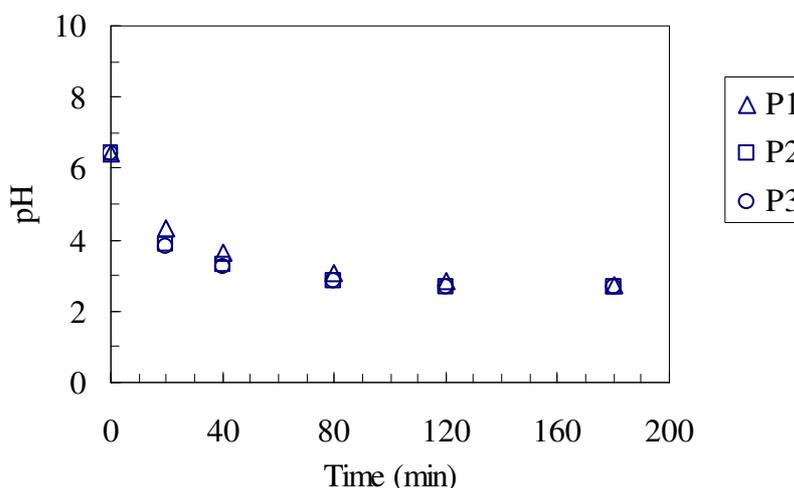


Figure 3. pH evolution with reaction time.  $[\text{Ph}]_0 = 1\text{g}\cdot\text{L}^{-1}$ , Ph: $\text{H}_2\text{O}_2$  molar ratio = 1:14,  $T=30^\circ\text{C}$ . Reaction time = 3h.

In addition, the conversion of hydrogen peroxide was evaluated during reaction. Results are presented in Figure 4. The  $\text{H}_2\text{O}_2$  decomposition rate was higher for the

catalysts with two or three impregnations steps (P2 and P3) than for the catalyst with just one impregnation cycle P1. This is because the production of  $\text{OH}\bullet$  radicals strongly depends (among other factors) on the amount of copper present in the system.

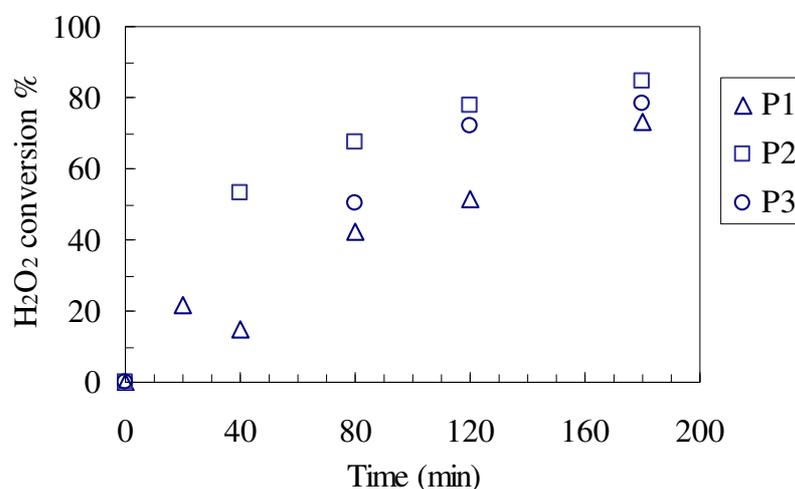


Figure 4.  $\text{H}_2\text{O}_2$  conversion vs time.  $[\text{Ph}]_0 = 1\text{g}\cdot\text{L}^{-1}$ ,  $\text{Ph}:\text{H}_2\text{O}_2$  molar ratio = 1:14,  $T=30^\circ\text{C}$ . Reaction time = 3h.

Used catalyst P1, P2 and P3 were further characterized by atomic absorption to measure the amount of active phase after three hours of reaction. Results are presented in Table 2. As observed, leaching was significant for all the samples; therefore the occurrence of homogeneous reactions can not be ignored.

Table 2. Catalytic behavior for WPO of phenol

Sample	Initial Cu content ( $\text{mg}\cdot\text{g}^{-1}$ )	Phenol conversion at 180 min (%)	TOC conversion at 180 min (%)	Cu leached (%)
P1	20.4	100	74	50,5
P2	31.8	100	84	60,1
P3	33.3	100	83	58,3

### 3.3. TGA analysis

TGA results obtained with fresh and used catalysts are presented in Table 3. At the lower temperature range reported, weight loss can be attributed to the evaporation of liquid present in the catalysts (water in fresh samples and water, phenol, intermediate products in used samples). In the second range of temperatures studied ( $110^\circ\text{C}$ - $300^\circ\text{C}$ ), the weight loss is attributed to the decomposition of Chitosan.

Table 3. Percents of TGA consumed mass between ranges of temperature.

Sample	TGA – weight loss (%)	
	27°-110°C	110° - 300°
P1 fresh	24,3	5,4
P1 used	41,9	3,8
P2 fresh	8,4	6,2
P2 used	42,9	5,5
P3 fresh	9,7	6,6
P3 used	35,6	12,2

The differences between fresh and used samples could indicate that used samples have lost Chitosan during reaction, probably due to depolymerization reactions induced by the presence of hydrogen peroxide at acid conditions (Tian et al., 2004).

### 3.4. TPR analysis

TPR analysis was performed in fresh and used samples of catalyst P1 and in a catalyst based on CuCl<sub>2</sub> adsorbed onto  $\gamma$ -alumina. Results are presented in Figure 5. For Chitosan based samples, the presence of two reducible species was detected and assigned to species CuCl<sub>2</sub> and Cu-Chitosan complex. Results also showed a reduction on the amount of CuCl<sub>2</sub> and Cu-Chitosan complex present in the used sample, this effect is analogous to the results reported by AA.

Evaluation of TPR outcomes obtained with fresh catalyst P1 and the catalyst based on CuCl<sub>2</sub> adsorbed onto  $\gamma$ -alumina showed that the amount of CuCl<sub>2</sub> was higher for catalyst P1. This is in agreement with the ability of Chitosan to adsorb metal ions (Guibal, 2004).

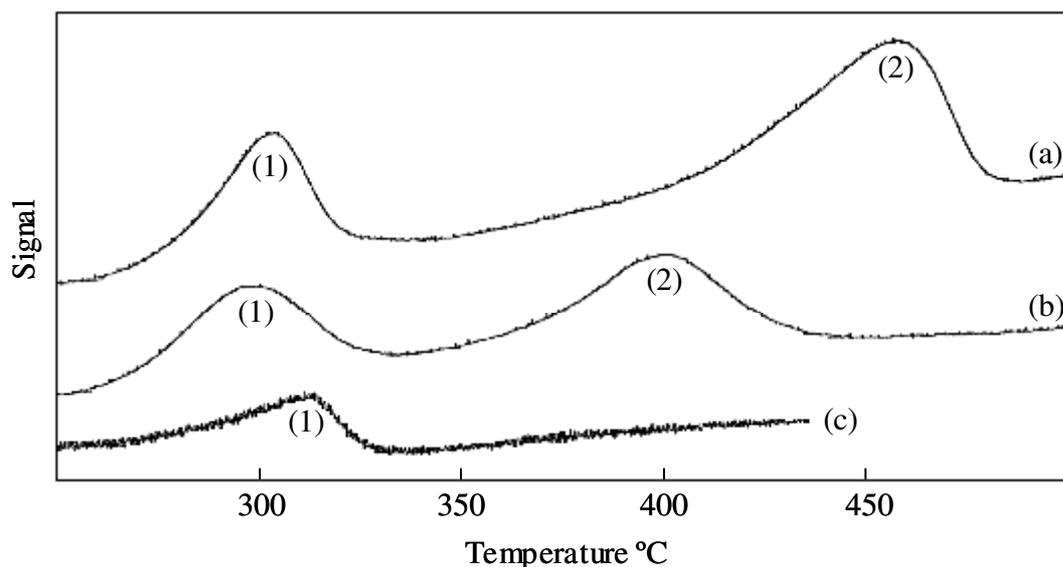


Figure 5. TPR profiles of two species (1) CuCl<sub>2</sub> and (2) Cu-Chitosan contained on (a) Fresh P1 catalyst, (b) Used P1 catalyst and (c) CuCl<sub>2</sub> supported onto  $\gamma$ -alumina.

## 4. Conclusions

The CWPO of phenol was studied using Cu-Chitosan composite catalysts obtained by coating Cu-Chitosan complexes onto  $\gamma$ -alumina in consecutive impregnation steps. Catalyst P1, P2 and P3 were prepared with one, two and three impregnation cycles. All samples showed phenol conversion up to 100% at room conditions. Moreover, TOC conversions of 80% were obtained, assuring a high phenol mineralization although the presence of refractory carboxylic acids can not be neglected.

Better performances were obtained with catalysts P2 and P3, which had approximately the same copper content.

For all the samples, leaching of copper and loss of Chitosan was detected.

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