

# OXIDATION OF PHENOL IN AQUEOUS SOLUTION WITH COPPER OXIDE CATALYSTS SUPPORTED ON $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, PILLARED CLAY AND TiO<sub>2</sub>: COMPARISON OF THE PERFORMANCE AND COSTS ASSOCIATED WITH EACH CATALYST

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**Abstract** - The Catalytic Wet Air Oxidation (CWAO) of phenol using copper oxide catalysts supported by  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and pillared clay was evaluated to identify which of these catalysts was the most appropriate for this reaction. The CuO/PILC, CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/TiO<sub>2</sub> catalysts were the most successful at removing phenol and resulted in more than 96% conversion. Among these catalysts, CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> produced the largest amount of CO<sub>2</sub>, the lowest amount of intermediate products and the lowest amount of copper leaching. These results showed that the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was the best for the end of the reaction. However, the methods used in this study did not allow us to identify the most appropriate reaction time (or catalyst). An alternative approach for this problem was to quantify the costs for each reaction time. Using this approach, the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was the most economically favorable catalyst when it was used during the first hour of the reaction.

**Keywords:** Phenol; Oxidation; CuO; Pillared clay; TiO<sub>2</sub>; Costs.

## INTRODUCTION

The elimination of organic pollutants in wastewater by oxidation is an important subject that deserves particular attention due to increasing amounts of industrial and urban emissions and the increasing need to protect the environment.

Phenolic compounds form a class of chemical species that are commonly found in wastewaters from numerous industries. These compounds are dangerous to living organisms due to their high levels of toxicity.

Conventional industrial effluent treatments are unable to reduce phenolic concentrations to accept-

able levels. Although biological treatment is increasingly effective due to the progress of microbiological studies, according to Nogueira (1998) and Kim and Ihm (2011), microbial intolerance to these compounds remains an issue. Quintanilla *et al.* (2010) rejected the possibility of sending effluents directly for biological treatment and noted the need for pre-treatment in an integrated process for increasing biodegradability.

In this context, Advanced Oxidation Processes (AOPs) may generate good results for the environment. According to Kim and Ihm (2011), the Catalytic Wet Air Oxidation (CWAO) process is most commonly used by petrochemical, chemical and

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pharmaceutical industries. Gao *et al.* (2013) reported that the CWAO process is effective at eliminating organic and inorganic pollutants in wastewaters and that units have been installed in chemical, petrochemical and pharmaceutical industries. According to Oliviero (2003), the CWAO process can treat many pollutants, including pollutants with low solubilities or those containing polymers and fatty acids. Kim and Ihm (2011) reported that the CWAO process at high pressure (1 to 7 MPa) and high temperatures (423 to 563 K) can reduce pollutant concentrations, such as phenolic compounds. Thus, the CWAO process it is one of the most efficient methods for reducing the Total Organic Carbon (TOC) concentrations in wastewater (Luna *et al.*, 2009).

According to Santos *et al.* (2005), the catalysts used in the CWAO process could be classified as being composed of noble metals (Ru, Pd, Pt), metallic oxides and their complexes (Cu, Zn, V, Mn/Ce, etc.). Copper oxide-based catalysts have been widely researched in the last 35 years due to their high activity. However, the dissolution of copper catalysts in acidic environments is well known (Sadana and Katzer, 1974). In studies conducted by Pintar (1997), phenol was oxidized over a supported Zn-Cu-Co oxide catalyst, resulting in the dissolution of metals, including 20% Cu, 10% Zn and 15% Co. According to Pintar and Levec (1992a), these species can increase the global disappearance rate of phenol by 10% when they are dissolved in the liquid phase. Arena *et al.* (2003) revealed that dissolved copper ions from catalysts produce an important reaction extension in the liquid phase that changes the heterogeneous catalytic reaction into a homogeneous reaction and influences the oxidation rate of organic compounds and their oxidation routes. Among the materials studied,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is one of the best (Massa *et al.*, 2009). Other support materials, such as silica (Njiribeako *et al.*, 1978), activated carbon (Brainer *et al.*, 2014), pillared clay (Carriazo *et al.*, 2005), TiO<sub>2</sub> (Dükkancı and Gündüz, 2009), MCM-41 (Eimer, 2006), ZSM-5 (Valkaj *et al.*, 2007), Ce and Ce-Zr oxides (Nousir *et al.*, 2008),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (Balzer *et al.*, 2014) and polymeric membranes (Molinari *et al.*, 2009), are promising materials and are being increasingly used as catalytic oxidation supports.

Generally,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, pillared clay and TiO<sub>2</sub> have been shown to be adequate for supporting copper oxide when applied to the phenol catalytic oxidation process. However, no studies have indicated which of these catalysts is best. Therefore, the aim of this study is to determine the relevant aspects that contribute to the classification of CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CuO/PILC and CuO/TiO<sub>2</sub> catalysts in the CWAO of phenol.

This paper proposes a method that uses information about the costs involved in catalyst preparation, the removal of metals and the removal of organic intermediates to define the importance of these catalysts.

## MATERIALS AND METHODS

### Preparation of the Catalysts

The catalysts used in this study were prepared using the impregnation method (Hamad, 2010) with a copper nitrate aqueous solution to obtain catalysts with 3% w/w copper oxide supported by TiO<sub>2</sub> (Fluka), Al<sub>2</sub>O<sub>3</sub> (Degussa) and Montmorillonite - Aluminum Pillared Clay (PILC) (Fluka). Using the following procedure, 5 g of each catalyst were prepared. First, 0.549 g of copper precursor (Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5 H<sub>2</sub>O, Sigma), was dissolved in 0.06 L of deionized water while maintaining the homogeneity of the solution using magnetic stirring. In another recipient, 4.55 g of the support material was added to 0.075 L of deionized water while maintaining the homogeneity of the solution using magnetic stirring. Then, the two solutions were poured into another glass vessel while maintaining the temperature at 393 K and stirring with a magnetic stirrer for 5 h. The resultant mud was dried in an oven at 393 K for 12 h. The solid matter obtained was ground, sieved and calcined at 673 K for 4 h at a heating rate of 274 K min<sup>-1</sup> under air at a flow rate of 0.498 L min<sup>-1</sup>. In addition to these materials, commercial copper (II) oxide (Sigma) was used as a catalyst.

### Catalyst Characterization

The copper (II) oxide content in the heterogeneous catalysts was determined using an X-ray fluorescence spectrometer XRF-1800 (Shimadzu).

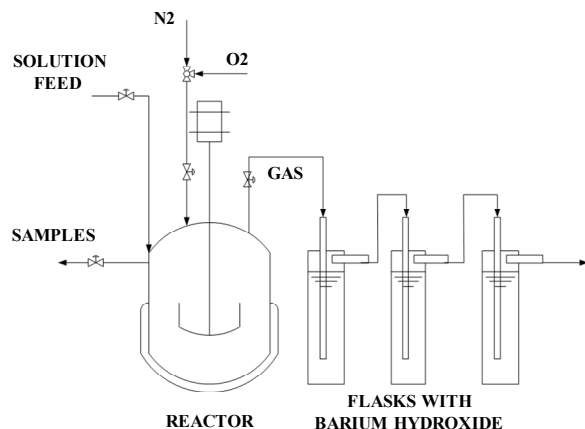
Qualitative information regarding the sample composition was obtained using Energy Dispersive X-ray Spectroscopy (EDX). In addition, a scanning electronic microscope was used (model LEO 440i (LEO)) with a secondary electron detector for micrographs, a Si/Li detector (Oxford) for elemental microanalysis and a sputter coater (Polaron). The samples were coated with Au/Pd and the working temperature was 288 K.

The specific surface areas were measured using the BET method, which involves the physisorption of gas multilayers on the particle surfaces. For this analysis, a Gemini 2375 was used and the samples were pre-treated under a vacuum at 573 K for 2 h to remove impurities from the catalyst, such as water, CO<sub>2</sub>, and CO.

The dissolution of copper(II) was analyzed using atomic absorption spectroscopy (Perkin Elmer Spectrometer model AAnalyst 100). Three standards were used to construct the calibration curve for each element and distilled water was used as a blank. Aliquots of the reaction mixture were vacuum filtered before atomic absorption spectroscopic analysis. Next, X-ray diffraction (XRD) measurements were carried out on a Shimadzu apparatus (XRD-6000) employing  $\text{CuK}\alpha$  radiation from  $5^\circ < 2\theta < 80^\circ$  with a scanning speed of  $2^\circ \text{ min}^{-1}$  to investigate the crystal-line structures of the catalysts. The angle range and the temperature rate were similar to those used by Manivel *et al.* (2010), Hamed (2010) and Achma *et al.* (2008).

### Experimental Set-Up

The experiments were carried out on a bench unit, which is illustrated in Figure 1. The reaction occurred inside a stainless steel reactor with a capacity of 0.399 L (Parr Instruments Co.). The reactor was linked to an agitator and a heating system, and the rotation and temperature were controlled by a Parr Instrument module (model 4842). The pressure control system was a model BRGDS (Autoclave Engineers).



**Figure 1:** Experimental set-up for the catalytic oxidation studies.

The oxidation reaction was carried out in a semi-batch slurry reactor that was operated in semi-continuous mode. First, the reactor was loaded with 0.180 L of distilled water and 0.2 g of catalyst. The system was closed and purged with  $\text{N}_2$  and  $\text{O}_2$  to draw out any contaminants that could influence the reaction. The pressure of the reactor was adjusted to  $2 \times 10^3$  kPa. After the mixture solvent/catalyst had reached its working temperature (413 K), 0.02 L of a phenol solution was added at  $50 \text{ g L}^{-1}$ , which resulted

in a reaction mixture with  $5 \text{ g L}^{-1}$  phenol (0.02% w/w) (according to Duprez *et al.*, 1996). Next, the reaction was started, and samples were collected each hour until 5 hours of processing were completed.

### Analytical Methods

The concentrations of the samples drawn from the reaction mixture were identified using gas chromatography. For this analysis, a TRACE GC (Thermo Quest) equipped with a NST150 capillary column (30 m; 0.25 mm DI; 0.25  $\mu\text{m}$ ) (Nano Separation Technologies), a FID detector and a quartz splitless liner with silanized glass were used to make the injector walls inert to the short chain carboxylic acids that formed during the course of the reaction. The chromatographic method was adjusted according to Aquino and Santiago-Silva (2006) with the injector and detector temperatures set at 523 and 573 K, respectively. Next, the oven was heated to 333 K and remained at this temperature for 1 min before increasing to 473 K at  $5 \text{ K min}^{-1}$ , where it remained for 1 min. Next, the system was calibrated using acetic acid and phenol with phenol concentrations of 0.1 to  $5 \text{ g L}^{-1}$  and acetic acid concentrations of 0.003 to  $0.03 \text{ g L}^{-1}$ . A calibration curve was constructed separately for each compound by plotting the peak area (y-axis) versus the concentration (x-axis). All curves were fit using a linear least-squares regression. The values obtained for the correlation coefficients were above 0.98 and the standard deviation was below 2.43%, which indicated that the method was linear in the studied concentration range.

The experimental error was calculated using the phenol concentrations at the end of the reactions. The average phenol concentration and the variance were calculated for each experimental test. The estimated weighted averages of the variances were obtained by using these variances and the degrees of freedom of each test. From these results, we obtained an experimental standard deviation of approximately 3.21% (which is also referred to as the standard error or experimental error) for the 95% confidence interval.

The  $\text{CO}_2$  produced by the phenol oxidation reaction was indirectly identified through the production of  $\text{BaCO}_3$ .

The gas generated from the oxidation reaction was continuously bubbled through 2 L of an aqueous solution containing  $11 \text{ g L}^{-1}$  of barium hydroxide and was stored in a serially arranged battery of washer flask. The  $\text{BaCO}_3$  formed was periodically collected and filtered, dried and weighed. Next, the amount of  $\text{CO}_2$  was defined using stoichiometry. The  $\text{Ba(OH)}_2$  concentration was calculated according to mass

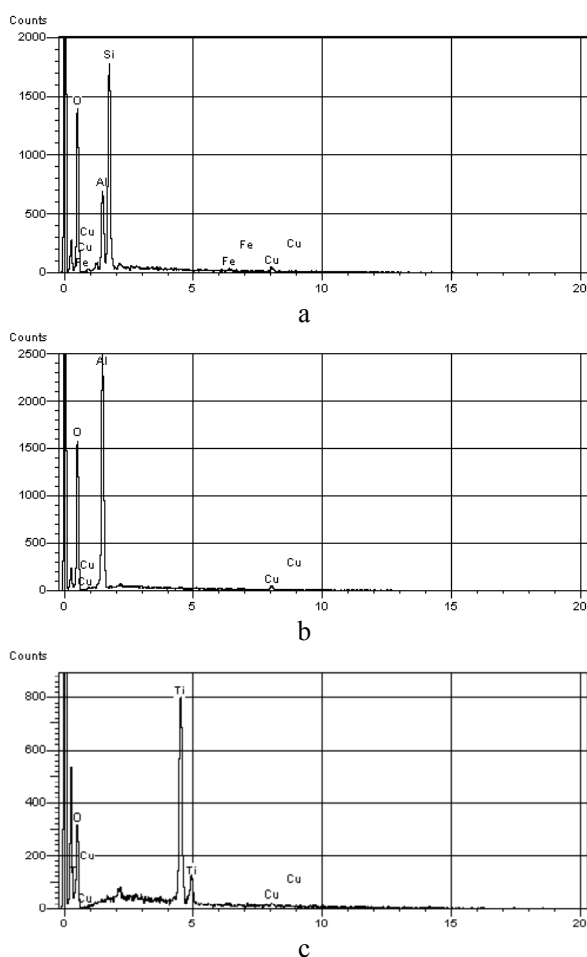
balance and by considering that the initial phenol content was completely converted to  $\text{CO}_2$ .

The intermediate products were estimated based on the carbon balance according to the mass of phenol after time  $t$  and the amount of  $\text{CO}_2$  generated during the process.

## RESULTS AND DISCUSSION

### Characterization

The EDX technique was used to identify the chemical composition of each catalyst, and the results of the analyses are shown in Figure 2.



**Figure 2:** The EDX patterns of (a) CuO-PILC, (b) CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$  and (c) CuO- $\text{TiO}_2$ .

The chemical compositions of the studied catalytic systems were typical of catalysts formed by copper oxides, particularly of those supported by pillared clay (Figure 2a), alumina (Figure 2b) and titanium dioxide (Figure 2c). Table 1 presents the

CuO content of each catalyst according to the XRF technique and their BET specific surface areas.

**Table 1: Copper (II) oxide contents and specific areas of the catalysts.**

Catalysts	CuO (% W/W)	BET ( $\text{m}^2/\text{g}$ )
$\text{TiO}_2$	-	8.1
CuO/ $\text{TiO}_2$	4.6	7.0
PILC	-	114
CuO/PILC	3.1	38.4
$\text{Al}_2\text{O}_3$	-	198
CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$	3.6	193
CuO	-	8.5

From the results, it is clear that the surface areas of the supports are distinct, potentially due to the structural characteristics of each material. A high surface area carrier is capable of accommodating a greater number of active sites, which would increase the possibility of its efficient application in catalysis. However, in most cases, a direct relationship exists between the surface area and the catalyst performance due to the lack of homogeneity of the catalyst surface energy.

The value obtained for the surface area of the  $\text{TiO}_2$  support was low relative to the values obtained for the surface area of the  $\text{Al}_2\text{O}_3$  support. The difference in surface area occurred because  $\text{TiO}_2$  has few pores and because particle agglomeration can occur in the pores, which further contributes to the reduction of the specific surface area.

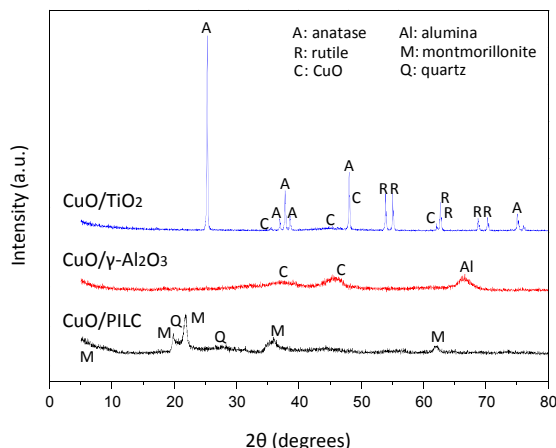
Furthermore, the presence of copper (II) oxide in the support structure potentially reduced the specific area due to the occupation of the pores by salt precursors. The most pronounced reduction in the surface area occurred when the pillared clay was impregnated, which resulted in a 66% reduction relative to the pure pillared clay. This reduction can be explained by observing the micropore volumes of each material ( $1.447 \times 10^{-3} \text{ L g}^{-1}$  for pillared clay and  $0.023 \times 10^{-4} \text{ L g}^{-1}$  for CuO/PILC). In addition, this result suggests that some Cu species may block the entrance to the porous network and/or occupy the inner pores of the Al-PILC during the preparation process and make it inaccessible. Similar events were reported by Barrega-Vargas *et al.* (2005) and Marinkovic-Neducin *et al.* (2004).

XRD was conducted to determine if any changes in the catalyst structures occurred, as shown in Figure 3.

The XRD patterns of the CuO- $\text{TiO}_2$  catalyst revealed the presence of anatase and rutile and the monoclinic crystal structure of CuO (Tenorite) (Yousef *et al.* (2012)).

The XRD pattern of the CuO- $\text{Al}_2\text{O}_3$  catalyst showed two major characteristic peaks for the CuO

particles. The peaks at 38.4° and 48.4° represented the crystal faces of monoclinic CuO. The presence of alumina was confirmed by the peak at 66.7°, which was a reflection from the alumina support (Nandanwar and Chakraborty, 2012).



**Figure 3:** XRD results for catalysts: CuO/TiO<sub>2</sub>, CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/PILC.

The XRD pattern of CuO/PILC showed peaks that were characteristic of clay and quartz (Wu *et al.*, 2011). The peak at 9° was attributed to the basal reflection and represents the distance between the two clay layers, including the thickness of one of the layers. The peaks at 18° and 35° were attributed to the two-dimensional (hk) planes, which resulted from the diffraction of the random stacking of the layers. The peaks at 21° were ascribed to quartz (Q) impurities in the clay. No characteristic peak of crystalline CuO was observed in these XRD patterns, which indicated that the copper species was well dispersed on the support (Li *et al.*, 2011).

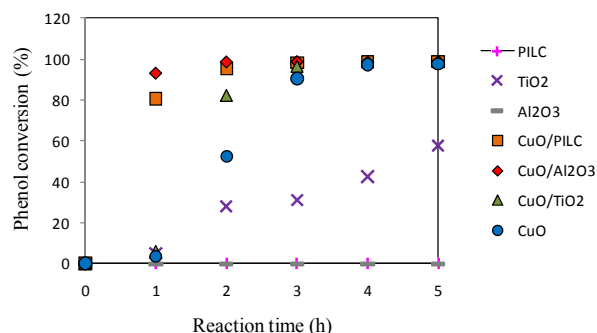
Additionally, the structures of the materials were preserved when compared with the XRD of the pure supports that were reported by Zhu *et al.* (2009) for TiO<sub>2</sub>, by Park *et al.* (2004) for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and by Su *et al.* (2009) for pillared clay.

### Catalytic Tests

Catalytic tests were carried out to identify which of the studied catalysts (CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CuO/TiO<sub>2</sub> and CuO/PILC, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, pillared clay and CuO) were more suitable for the catalytic oxidation of phenol in water. The process variables in the experimental tests included a temperature of 413 K, total pressure of  $2 \times 10^3$  kPa, catalyst concentration of 1 g L<sup>-1</sup>, phenol concentration of 5 g L<sup>-1</sup> and initial pH of approximately 5.

### Oxidation of the Phenol

Figure 4 shows that the CuO/PILC, CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/TiO<sub>2</sub> catalysts were the most successful at removing the phenol, which generated conversions of more than 96% in the first three hours after starting the reaction. The Al<sub>2</sub>O<sub>3</sub> and pillared clay catalysts were unable to remove the phenol, so the results are presented on the abscissa in Figure 4.



**Figure 4:** Variations in the phenol conversion as a function of reaction time for the catalysts.

The absence of activity in the pillared clay diverges from the findings of Carriazo *et al.* (2005), who recorded a conversion of above 90% two hours after starting the reaction. This result can be explained by the low iron content of the material that was used in this work (0.7% w/w) relative to the material used by Carriazo *et al.* (2005) (6.06% w/w).

The CuO and TiO<sub>2</sub> catalysts were active, producing a period of induction of approximately one hour. Most studies concluded that the reaction involved the generation of free radicals, which are responsible for the initial steps of phenol oxidation (Shibaeva *et al.*, 1969; Miguélez *et al.*, 1997). The curve generated by the TiO<sub>2</sub> indicates that the phenol was slowly eliminated, with a conversion rate of 58% in 5 h after starting the reaction. The oxidation reaction produced by the CuO went through a period of high activity and reached a conversion of 97% in 3.5 h after the start of the reaction.

The CuO catalyst showed a higher activity, likely due to the formation of free radicals, as explained by Sadana and Katzer (1974). The operating conditions of the process potentially favored the formation of cuprous oxide or phenolic radicals on the catalyst surface.

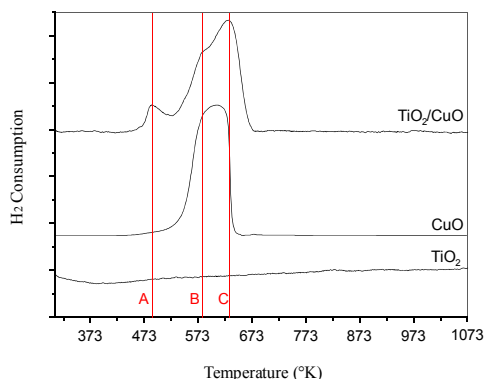
The CuO/TiO<sub>2</sub> and CuO catalysts showed similar induction periods in the first hour of the reaction. According to Table 2, the copper interaction with TiO<sub>2</sub> resulted in a higher reaction rate than CuO and

resulted in a greater activity (Figure 4), most likely because the synergy between CuO and TiO<sub>2</sub> decreased the amount of energy that was required to excite the electrons in the conduction band to the valence band (as explained by Manivel *et al.* (2010)).

**Table 2: Changes in the rate of reaction in the oxidation of phenol.**

Time (h)	Rate of Reaction (mol/L h)			
	CuO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	CuO/PILC	CuO/TiO <sub>2</sub>	CuO
1	4.99	4.49	0	0
0.5	4.99	4.49	0	0
1	4.99	4.49	1.06	0.53
1.5	0.29	0.75	4.27	2.45
2	0.29	0.75	4.27	2.45
2.5	0	0.08	0.54	2.45
3	0	0.08	0.54	2.45
3.5	0	0	0	0.31
4	0	0	0	0.31
5	0	0	0	0

Figure 5 shows the H<sub>2</sub>-TPR profiles of the CuO, TiO<sub>2</sub> and CuO/TiO<sub>2</sub> samples.



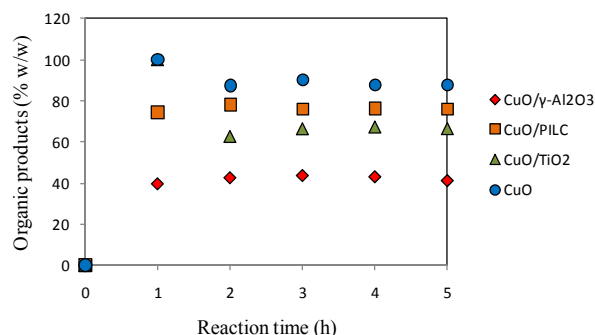
**Figure 5: TPR profiles of CuO, TiO<sub>2</sub> and CuO/TiO<sub>2</sub> samples.**

A single peak was observed at 325 °C for pure CuO. However, no peak was observed for pure TiO<sub>2</sub>, which indicated that the reduction of TiO<sub>2</sub> was very difficult. For CuO/TiO<sub>2</sub>, three reduction peaks were observed (A, B and C) at 213, 310 and 360 °C, respectively. According to Xiaoyuan *et al.* (2004), peak A likely resulted from the interaction of highly dispersed CuO species with TiO<sub>2</sub>. In addition, peak B likely resulted from oxide clusters with a structure that was similar to the structure of CuO (i.e., short-range order but not crystalline). The C peak potentially resulted from the CuO crystallites. According to Gaoa *et al.* (2011), compared with the crystalline CuO species, the dispersed copper oxide species are in close contact with the surface of TiO<sub>2</sub>, resulting in a strong interaction between them and in the lowest

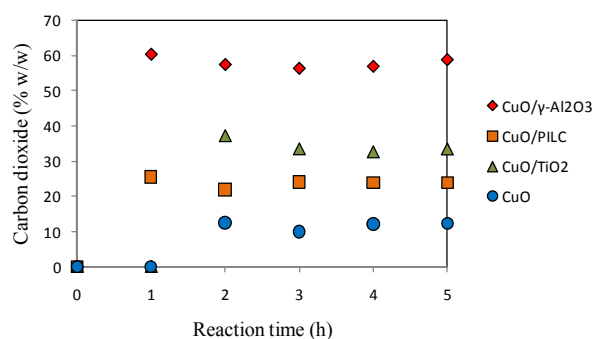
reduction temperature. Thus, it was suggested that the CuO species with high dispersion was an active site for phenol oxidation and that the improved catalytic activity was likely related to the highly dispersed CuO species.

According to Akyurtlu *et al.* (1998), the profiles of conversion presented by the CuO and CuO/TiO<sub>2</sub> systems indicated that no mass transfer limitations occurred between the gaseous phase and the liquid phase. For these authors, the induction period resulted from a very slow phase in the formation of hydroquinone and catechol, which suggested a mechanism of homogeneous-heterogeneous free radicals.

Figure 6 shows that more than 50% of the intermediate products formed during the reaction with CuO and CuO<sub>2</sub>/TiO<sub>2</sub> were present in the reacting mixtures. However, according to Figure 7, the CuO/TiO<sub>2</sub> system produced 22.5% more CO<sub>2</sub> than CuO, which indicated a better activity for total oxidation.



**Figure 6: Changes in the concentrations of the intermediate products during the oxidation of phenol.**



**Figure 7: Changes in the carbon dioxide concentrations during the oxidation of phenol.**

The interactions of copper with the alumina and the pillared clay produced more active materials than the interactions of copper with TiO<sub>2</sub>, even when the induction time generated by the CuO was eliminated. The CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/PILC materials presented

similar activities, with a slightly higher reaction observed for CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for up to two hours of processing, as shown in Table 2. These catalysts were the most efficient at eliminating phenol and resulted in a conversion of approximately 80% 1 h after starting the reaction.

During the first hour of the reaction, the phenol was degraded quickly in the presence of the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/PILC catalysts. The best CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> activities for the degradation of phenol were shared with the best activity for complete oxidation (to produce 50% w/w of CO<sub>2</sub>, as shown in Figure 7, and lower concentrations of intermediate products (37% w/w), as shown in Figure 6). However, despite the fact that the degradation of phenol was high when using the CuO/PILC catalyst, the activity was not good enough for complete oxidation (21% w/w CO<sub>2</sub>) and the intermediate product degradation was not good (67% w/w). This result can be explained by the greater available surface area in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as shown in Table 1, and the greater mass of CuO that remained on the surface after leaching, as shown in Table 3. When analyzing the data using PILC, the surface area of CuO/PILC was much smaller than the surface area of the clay. In addition, the mass of copper that remained on the catalyst surface after leaching was the lowest. These results suggest that the CuO/PILC catalyst may provide better results, although the surface area was greatly reduced during the preparation phase (63% reduction) and the amount of copper leaching was very high (72%).

### Dissolution of Copper

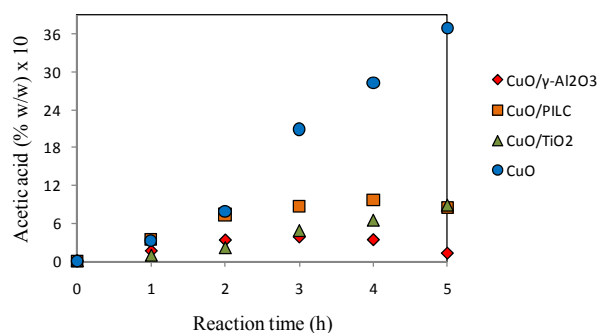
The dissolution of copper on the surface of the catalyst occurred when the catalyst was exposed to the hot and acidic aqueous media. According to Pintar and Levec (1992b), the exposure of the catalyst to the hot and acidic aqueous medium favored an increase in the copper solubility. The loss of this metal to the aqueous environment not only influences the stability of the catalyst, but also modifies the reaction mechanism by altering the phenol reaction rate and the rate that intermediates are generated due to oxidation (Santos *et al.*, 2005). In addition, Pintar (2003) observed that the reaction characteristics were attributed to the copper in solution and that the increase in toxicity should be considered when using this metal as a catalyst. To investigate the increase in toxicity that results from the dissociation of copper from the catalysts used in this study, the copper contents in the reaction mixtures were analyzed and are presented in Table 3.

**Table 3: Dissolution of copper on the catalyst surface 5 h after the beginning of the reaction.**

Catalysts	Copper			Dissolution (% w/w)
	New catalyst (g)	Solution		
		(g)	mg/L	
CuO/TiO <sub>2</sub>	0.0074	0.0048	24	64.9±2.35
CuO/PILC	0.0050	0.0036	18	72.0±2.35
CuO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.0058	0.0032	16	55.2±2.35
CuO	0.0048	0.0038	19	79.2±2.35

By analyzing the copper contents in the solutions, we observed that the metal concentrations for all catalytic systems were well above 1 mg/L, which is the concentration required by Brazilian law (CONAMA). The high concentration of copper in the aqueous solution can be explained by its low concentration on the surface of the new catalyst (3% w/w), as reported by Garcia *et al.* (2006). According to these authors, a small amount of copper is dispersed on the catalyst surface without causing any copper agglomerates, which facilitates the action in acid environments and causes increased leaching. When analyzing the percentage of copper in the aqueous solution, we observed that the catalytic systems underwent extensive leaching based on the operational conditions that were used. The largest loss occurred when using the CuO/PILC catalyst, which resulted in a 72% loss of its original copper mass. However, the other catalysts also underwent intense leaching, with losses that exceeded 50%.

Table 3 can be compared with Figure 6 to explain the variations in the dissolved copper concentration. The influences of the catalysts on the production of the intermediate products follow the same order as copper dissolution (CuO > CuO/PILC > CuO/TiO<sub>2</sub> > CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Thus, the amount of carboxylic acid in the reaction mixture follows the same trend-line, which is confirmed by the production of acetic acid (shown in Figure 8).



**Figure 8: Changes in the acetic acid concentrations during the oxidation of phenol.**

The acidity of the reaction medium was largely generated by the carboxylic acids that existed in the reaction mixture. Greater acid concentrations corresponded with lower pH values in the reaction mixture and greater copper leaching. Thus, the increased leaching that occurred as the concentrations of the intermediate products increased in the medium can be explained.

### COST OF THE REACTION

To choose the most suitable catalyst for the CWAO process, the catalytic activity results and the total cost of the process must be considered. In this study, the cost of the catalyst separation from the suspension at the end of the reaction, the fixed costs associated with the equipment, and the operational costs were considered to be similar for all catalytic systems and were labeled as FC. The FC cost was considered as a reference cost and was removed from the total cost. Thus, the total cost was the sum of the costs that varied with the reaction time and the costs of the fresh catalysts. All tests were performed using fresh catalyst, which is reflected in the cost. The advantages and disadvantages of using regenerated catalysts were not considered in this work.

The costs involved, such as the cost of producing fresh catalysts (CPC), the cost of removing metals from the liquid phase (CML) and the costs of disposing of the organic products that were not degraded in the CWAO process must be considered. The cost of removing organic products from the reaction mixture (0.2 L) was labeled as EFC (the cost of removing the phenol) and CIP (the cost of disposing of the intermediate products). The costs related to the consumption of oxygen and nitrogen (CON) and electricity (CE) per 0.2 L of the reaction mixture were included because they were not the same for each maximum conversion. With these considerations, the total cost for each catalyst used per 0.2 L of the reaction mixture is given by using Equation (1).

$$\text{CUT} = \text{CPC} + \text{CML} + \text{EFC} + \text{CIP} + \text{CON} + \text{CE} \quad (1)$$

Tables 4, 5 and 6 show the basic costs that were considered in this work. The cost of producing the catalysts (CPC) was calculated from the cost of the raw materials. The costs of removing the metals from the liquid phase (CML), the phenol (EFC) and the intermediate products (CIP) were defined as described by Santos (2002a). Santos (2002a) used data from the World Bank (1992), which shows the costs of removing contaminants from industrial effluents

( $0.5 \times 10^{-3}$  US\$ at  $2.0 \times 10^{-3} \text{ g}^{-1}$  of COD and 0.07 US\$ at  $0.175 \text{ g}^{-1}$  of metal) considering a pollutant load removal of 80%. The cost of removing the COD and dissolved copper used in this work were higher than the ranges shown when considering the industrial wastewater treatment as the most critical.

**Table 4: Cost of preparing the catalysts.**

Catalysts	Catalysts mass/test (g)	Cost (US\$)/test
CuO/PILC	0.2	0.26
CuO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.2	0.07
CuO/TiO <sub>2</sub>	0.2	0.34
CuO <sup>1</sup>	0.006	0.02

Note: <sup>1</sup>CuO mass is 3% of the heterogeneous catalysts.

Equation (2) was used to determine the chemical oxygen demand (COD), i.e., the amount of oxygen required to completely oxidize the organic products. A similar equation was used by Santos *et al.* (2002b) to determine the COD of the intermediate products during the catalytic oxidation of phenol in the aqueous phase.

$$\text{COD} = 8 (4X + Y - 2Z) / (12X + Y + 16Z) \quad (2)$$

The terms X, Y and Z refer to the number of carbon, hydrogen and oxygen atoms in the organic product (C<sub>X</sub> H<sub>Y</sub> O<sub>Z</sub>). The results from equation 2 are shown in Table 5, and the COD of the intermediate product consists of the average COD of the major solution components, except for phenol, which has a much higher COD than the other components.

**Table 5: Cost of treating wastewater containing organic products and copper.**

Species	g COD/ g organic product	Cost (US\$)
Copper	-	0.0175/g of metal
Phenol	2.38	0.0020/g of COD
Intermediates Products	1.19	0.0020/g of COD

The costs of preparing the catalysts were the same for all of the tests that were performed and were greater than the cost of removing phenol, the intermediate species and the copper from the reaction mixture. Furthermore, the mass of each contaminant was small due to the reaction conditions. Consequently, the cost of removing the pollutants represented a small portion of the total cost.

The costs of oxygen (and nitrogen) and electricity are shown in Table 6. The average costs of oxygen and nitrogen were based on the consumption of these

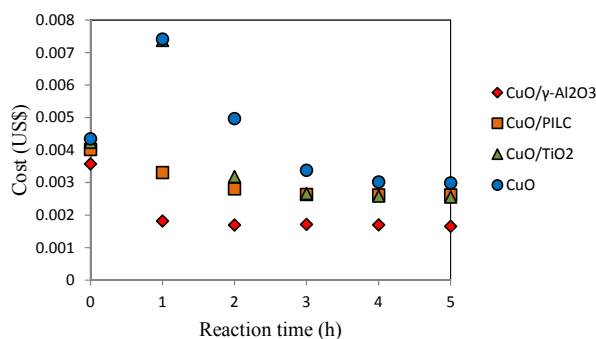


gases during the reaction and on their commercial values. The electricity cost was based on an average rate for Brazilian industries. According to the Brazilian Agency on electrical energy ANEEL (2014), a rate of US\$ 0.11/kWh (kilowatt-hour) was considered in this study.”

**Table 6: Accumulated costs of oxygen, nitrogen and electricity consumption.**

Reaction time (h)	Cost (US\$) Oxygen and nitrogen	Cost (US\$) electricity
0	0.50	0.022
1	0.52	0.044
2	0.54	0.088
3	0.56	0.132
4	0.58	0.176
5	0.60	0.220

The cost of preparing the catalyst is important for studying any reaction process. However, this cost can hide details of the process that are important for choosing the catalyst and can go unnoticed, given the significance of this cost. Figure 9 shows the initial cost evaluations when only considering the costs of removing pollutants from the reaction mixture. The costs presented throughout the reaction increase in the following order: CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < CuO/PILC < CuO/TiO<sub>2</sub> < CuO.

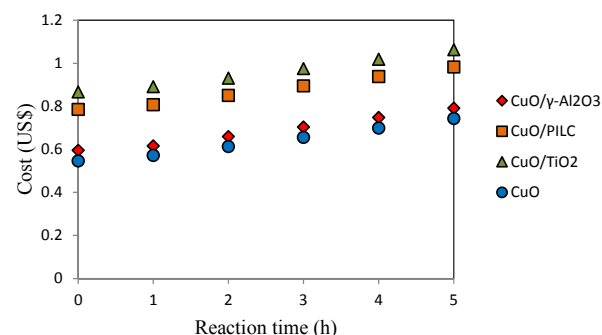


**Figure 9:** Process cost as a function of reaction time for the catalysts proposed in this study, excluding the catalyst, electricity and oxygen costs.

The costs of the CuO and CuO/TiO<sub>2</sub> catalysts increased during the first hour of reaction because the reaction media has high concentrations of phenol and dissolved copper relative to the other catalysts. From the third hour until the end of the reaction, the catalyst costs remained constant because the system was already in a steady state (i.e., the system reached maximum conversion). Initially, all of the costs shown in equation 1 were low and did not appear to influence the total cost. However, these costs in-

creased in importance with the scaling up of the reaction system.

Figure 10 shows the total costs involved in processing phenol (CUT).



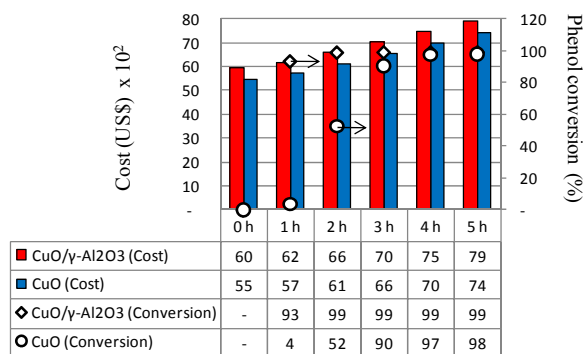
**Figure 10:** Total reaction cost.

Changes were observed in the shape of the curves and as the catalyst costs increased (CuO < CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < CuO/PILC < CuO/TiO<sub>2</sub>). The change in the behavior of the costs involved in the process can be explained by the cost of preparing the catalysts, whereas the costs of oxygen consumption and nitrogen and energy are the same for every hour of the reaction. A comparison of the ordinates in Figure 9 with those in Figure 10 reveals that the cost of catalyst preparation is at least 78 times the cost of the disposal of the organic products and copper from the reaction mixture. Thus, it is important to consider the costs of the catalyst, the costs of electricity consumption and the costs of gas consumption (O<sub>2</sub> and N<sub>2</sub>), along with the conversion of the main parameters for selecting the most appropriate catalytic system for the oxidation of phenol.

The best catalytic system for the CWAQ process for phenol should be chosen based on the low cost of the process and the high conversion rate of phenol. The conversion of CO<sub>2</sub> was indirectly considered in the intermediate costs of the organic products (i.e., CO<sub>2</sub> was produced because the intermediate products were consumed in the reaction). Figure 11 shows the cost data and the conversion of phenol for the CuO and CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

Information regarding the CuO/PILC and CuO/TiO<sub>2</sub> catalysts was not considered because their lower costs for maximum conversions outweigh the higher costs of the CuO and CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The conversion of phenol assigned to the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was 0.93 during the first hour of the reaction. However, the CuO catalyst provided a conversion of 0.9 (considered similar) in the third hour of the reaction. If these conditions were desired in the conversion process, the costs involved in these tests would be

practically the same, 0.62 US\$ and 0.65 US\$, with a slight advantage for the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (0.62 US\$). Namely, the two catalysts satisfy the oxidation process under these conversion conditions. However, if the desired conversion was approximately 0.99, the use of the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst would satisfy this condition within two hours of reaction at a cost of 0.66 US\$ for each test run. In addition, the CuO catalyst would reach a conversion of approximately 0.98 within five hours of reaction at a cost of 0.74 US\$ for each test run. For this last condition, the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is the most appropriate for the CWAO process of phenol.



**Figure 11:** Conversion and total cost of the reaction.

Although the total costs appeared to be very similar between the tests, the costs refer to a reaction mixture of 0.2 L. As the reaction volume increases, the difference between the costs also increases, making it evident that the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was the best in terms of costs and efficiency.

## CONCLUSIONS

The CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst appears to be the most appropriate for removing phenol from industrial effluents when considering its costs for a similar efficiency. However, pillared clay supported copper oxide is a promising catalyst, mainly due to its high phenol conversion, despite undergoing a significant reduction in specific area during its preparation and despite undergoing high copper leaching into the liquid medium.

The surface area reduction could be minimized using another impregnation method (for example, amorphous-citrate route or deposition precipitation) to improve the binding capacity of the copper on the surface of the pillared clay. Therefore, the greater surface area of the catalyst could contribute to a greater number of active sites available for reaction.

The method used to calculate the costs of processing phenol in this work are simple and appropriate for identifying the most suitable catalytic system. For the studied reaction system, the costs were determined throughout the reaction time, highlighting the optimal reaction time for each catalytic system. The results of this study showed that the oxidation of phenol is more economically favorable when using the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

However, it is possible that the commercial value of the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is greater than the cost of preparation shown in this work, which is the sum of the raw material costs. When the commercial prices of the catalyst are presented, perhaps another catalyst would be more suitable for the CWAO process of phenol.

## NOTATION

CUT	total cost
CPC	cost of the production of catalysts
CML	cost of the removal of metals from the liquid phase
EFC	cost of the removal of phenol
CIP	cost of disposing of intermediate products
CON	costs related to the consumption of oxygen and nitrogen
CE	costs related to the consumption of electricity
COD	chemical oxygen demand
PILC	pillared clay
AOPs	advanced oxidation processes

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