Polymer supported copper catalysts for aqueous phenol oxidation

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Abstract
Catalytic wet oxidation processes at laboratory conditions are classified into homogeneous and heterogeneous systems, although the catalyst at homogeneous systems has a recovery problem after utilization. Heterogenisation of homogeneous Cu\textsuperscript{2+} catalysts was achieved by adsorption of Cu\textsuperscript{2+} salts onto polymeric matrices. These polymer-supported-copper catalysts were tested on the catalytic oxidation of phenol at 30°C and atmospheric pressure using air and H\textsubscript{2}O\textsubscript{2} as oxidants. The catalytic active sites are represented by Cu\textsuperscript{2+} ions and showed to conserve their reduction quality in heterogeneous catalysis as well as in homogeneous system. The catalytic deactivation was evaluated by quantifying released Cu\textsuperscript{2+} ions in solution after oxidation occurs. Results indicate that Cu-P4VP 25% has a catalytic activity comparable with commercial catalyst, even more the leaching degree of 5 mg·l\textsuperscript{-1} supports Cu-P4VP 25% as the best option between tested catalysts.

Key-words: adsorption - poly(4-vinylpyridine) - chitosan - phenol oxidation

Introduction
Water is an indispensable substance for life but at the same time it is a limited natural source and the availability of water for human consumption is a constant problem. About 97% of water belongs to the oceans and 3% is fresh water. Moreover 0,3% of fresh water is distributed in lakes (87%), swamps (11%) and rivers (2%). The actual world volume of fresh water in use is 3.830 km\textsuperscript{3} per year and Europe has 418 km\textsuperscript{3} per year with 9,100 m\textsuperscript{3} per capita as (FAO, 2005) reports. Statistics present a deficit on water resources that increase difficulties for the economic development of Spain. Among the wide variety of water pollutants, phenol and its derivatives released from pharmaceutical, plastic, chemical and petrochemical industries have become an important environmental water pollution as (EPER, 2004) said. In many cases, biological depuration is enough and the best decision from an economically point of view. However most of wastewater coming from industrial effluents contains compounds poorly degradable. Phenolic compounds present a strong bacterial effect even at mild concentrations. In addition, most of phenol derivatives are contemplated as pernicious for health. According to Policy of (EPER, 2004), production of phenolic effluents in Europe in 2001 was capable to contaminate 14 millions of cubic meters of water at not permissible levels. To solve effluent treatment problems exists a variety of chemical processes like the Wet Air Oxidation (WAO) technology that involves the liquid-phase oxidation of organic compounds using air as oxygen source at high temperatures (200-350°C) and elevated pressures (20-200 bar). The efficiency of aqueous phase oxidation can be largely improved by the use of catalysts. Updated techniques for Catalytic Wet Air Oxidation (CWAO) present interesting characteristics at softer conditions, as (Fortuny et al., 1999) reported, than WAO with temperatures between 120 and 160°C and air pressures between 6 and 12 bar. In contrast, the catalysts present low stability and high costs. Then, the key points of CWAO are the stability of catalysts and the catalytic
recycling on homogeneous systems. At the end, CWAO compared with WAO states that the use of catalysts offers oxidation improvements and promotes lower energy requirements (Pintar, 2003) but longevity of catalyst is not assured. Fenton treatments (Bigda, 1995) work at lower conditions, presenting good results. There are some recent works that predict a rapid and total destruction of phenolic compounds by using hydrogen peroxide with ferric catalysts (Gupta, 2002). These processes are limited when the operations are continuous and when it is necessary a post-step to separate the catalyst from the oxidative media. Alternatively, an updated catalytic technology is proposed and refers the use of polymer-supported-catalysts at room temperature and pressure.

Previous works demonstrated that active metal salts, used as homogeneous catalysts, are capable to promote effectively the oxidation of recalcitrant compounds (Yamashita et al., 1988) moreover the catalytic activity of Cu$^{2+}$ for homogeneous catalysis is greatly enhanced when H$_2$O$_2$ is the oxidant (Maurya and Sikarwar, 2006). Additionally, these salts can be heterogenised by adsorption onto a large variety of supports as the polymers. The heterogenisation of homogeneous catalysts present great advantages due to the easy separation of the catalyst from the reaction media and the application on continuous processes (Louloudi, 2003). The use of synthetic and natural polymers for specific stabilization of active sites permits the combination of a wide range of properties that could meet current industrial needs (Kucherov, 2003). The chitosan, a polysaccharide biopolymer isolated from shellfish is a new class of potentially inexpensive and environmentally friendly substance that exhibits a high specificity towards metal ions as Guibal stated (2005).

This research is devoted to perform and promote the biodegradability of phenol, as model pollutant, by using the heterogeneous catalytic oxidation. The proposed technology develops the oxidation of phenol at mild conditions in a batch stirred tank reactor where the catalyst is a metal supported on a polymer. The study performs the immobilization of Cu$^{2+}$ ions onto different polymeric materials like poly(D-glucosamine) (Chitosan) and poly(4-vinylpyridine) (P4VP) by evaluating their adsorption capacities, then, the catalysts prepared are tested by running the catalytic oxidation of phenol, using air and hydrogen peroxide as oxidants. The process is devoted, in any case, to provide the demanded biodegradability to be sent to a WWTP and is not seen as an end treatment.

2. Methodology

2.1 Adsorption process

The adsorption of Cu$^{2+}$ ions were performed in a batch reactor at different temperatures (20, 30 and 40°C). Copper sulphate pentahydrated (CuSO$_4$.5H$_2$O, reference 61245) was purchased from Sigma-Aldrich, as well as poly(4-vinylpyridine) 2% cross-linked powder (P4VP 2%) (reference 81391) and poly (4 vinylpyridine) 25% cross-linked (P4VP 25%) (reference 81393). The Chitosan beads were supplied by Dr. E. Guibal (Laboratoire de Génie de l’Environnement Industriel, Ecole des Mines d’Alès, France). The beads were synthesized according to an original procedure (Guibal, 2005) and stored in a solution of NaOH. The beads were cleaned with distilled water before sorption process. The commercial copper catalyst 10% of CuO supported on γ-Al$_2$O$_3$ was provided by Harshaw (reference Cu0803 T1/8). In order to obtain the adsorption isotherms, Cu$^{2+}$ solutions were prepared at different initial concentrations (2400, 4800, 6000, 7200, 9600 and 12000 mg·l$^{-1}$) using CuSO$_4$.5H$_2$O salt dissolved in mili-Q water. The adsorption was carried out by pouring 1g of support (P4VP 2%, P4VP 25% or Chitosan) into 200 ml of Cu$^{2+}$ solutions. During the adsorption process, the variation of copper concentrations was monitored as a function of time. Adsorption was performed for a period of 24 hours until the highest adsorption capacity of each support was reached. Every 4 hours, samples of 10 ml were taken, centrifuged during 10 minutes in order to settle particles in suspension coming from the support, analysed by UV-Vis spectrophotometer at 800 nm of wavelength in the visible range and finally refilled into each batch reactor in order to maintain the initial volume. Once equilibrated adsorption is achieved, the catalysts are recovered by filtration, then cleaning with distilled water, dried at room temperature and stored in a dry container.

The adsorption behaviour reflects differences of exposed adsorption areas and polymeric structures used as supports. The adsorption capacity of P4VP 2% at 20, 30 and 40°C is remarkable higher than P4VP 25% and Chitosan. The characterisation of these polymers can be found elsewhere (Castro 2006).
2.2 Oxidation process

The oxidation assays were conducted at low temperature (30°C) and at atmospheric pressure in a batch stirred tank reactor of 180 ml and the initial phenol concentration was always 1000 mg·l⁻¹. Phenol crystallised (reference 144852) was purchased from Panreac with 99 to 105% of purity. Millipore mili-Q deionised water was used for all reagent solutions. Air and hydrogen peroxide were used as oxidants. When air was the oxidant, saturated air was bubbled into the reactor with a flow of 85 ml·min⁻¹ at the reaction temperature. When H₂O₂ was the oxidant, three different phenol/peroxide (Ph/H₂O₂) molar rates (1:1, 1:5 and the stoichiometric 1:14) were used. The mass of catalyst utilised was calculated to have 5, 10, 50, 100 and 200 mg Cu·l⁻¹ in solution. The pH was controlled along the reaction time. Reaction was monitored by taking samples of 1ml at the 5, 20, 40, 60 and 120 min and analysed by HPLC to determine the remaining the amount of phenol. Finally, TOC of 120 min samples was performed.

2.3 Analytical Procedure

Phenol conversion was determined measuring the phenol concentration in taken samples by HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS). The analyses were performed with a mobile phase with a gradient mixture of methanol and ultra pure water (Milli-Q water, Millipore) from 0/100% to 40/60%. The flow rate increases from 0.4 to 1.0 ml·min⁻¹). The pH of the water was adjusted at 1.4 with sulphuric acid (H₂SO₄). The detection was performed by UV absorbance at a wavelength of 254 nm. Automatic injector analysed volumes of 20 ml per sample. Calibration curve of phenol was also made using aqueous samples of known composition. TOC is analysed by a Total Organic Carbon Analyser (Analytic Jena,<model NC 2100). Samples are acidified with 50 ml HCl 2N then are bubbled with synthetic for 3 minutes to eliminate the inorganic carbon content. Afterwards, 100 ml of sample passed trough an oven at 800°C of temperature where organic carbon becomes CO₂ to finally be detected and reported.

3. Results and discussion

3.1 Homogeneous catalysis

In a first step, homogeneous catalytic oxidation of phenol was evaluated at two temperatures (30 and 50°C), with two Cu²⁺ salts (chloride and sulphate). The experiment realised a 30°C had a Ph/Cu²⁺ molar ratio of 1:1 and the experiment realised at 50°C a molar ratio of 1:10 in order to enhance the phenol conversion. The results of phenol conversion of these experiments are presented in Figure 1.

As it can be seen in the figure, the phenol conversion achieved at 30°C is less than 5% and is not suitable. For the second case, at 50°C, the phenol conversion was not improved with the new ratio. The reaction time was increased to 20 hours in order to attain higher phenol conversion. The conversion obtained after 20 hours, 20%, is not suitable in a continuous process as the oxidation rate is very small and was not quantified. On the other hand the Cu²⁺ concentration on the reaction solution was very high and would not be admitted as wastewater influent in any WWTP. As the results using air as oxidant were not suitable, it was decided to promote the reaction using heterogenised catalysts or using a more powerful oxidants as the hydrogen peroxide.

The second step carried out was the evaluation of the influence of H₂O₂ as oxidant agent. Three different Ph/H₂O₂ molar ratios were tested (1:1, 1:5 and 1:14) with four different Cu²⁺ concentrations (5, 10, 50, and 200 mg) at 30°C of temperature.
Figure 1. Homogeneous catalytic phenol oxidation at different temperatures and reaction time (30°C, 2h; 50°C, 24h). Influence of Cu²⁺ salts. \([\text{Ph}]_0=1 \text{ g l}^{-1}\). Air flow rate=85 ml·min⁻¹.

Figure 2 presents the results of phenol conversion using \(\text{H}_2\text{O}_2\) as oxidant agent at these conditions. The reaction arrived at equilibrium in between the first 5 minutes and was clearly improved when \(\text{H}_2\text{O}_2\) feeding was high. As it can be observed in the figure, at the stoichiometric 1:14 Ph/\(\text{H}_2\text{O}_2\) molar ratio, phenol disappearance achieves 90% using 50 mg of Cu²⁺, while using 200 mg of Cu²⁺, 95% is obtained. From this it can be demonstrated that phenol oxidation at homogeneous phase gives positive results when initial Cu²⁺ concentration increases as it was stated by Aguiar and Ferraz (2006), but also suggest the at high Cu²⁺ concentrations phenol conversion tends to be similar. The overactive catalytic activity of high Cu²⁺ concentrations among hydrogen peroxide produces an excess of \(\text{OH}^\bullet\) radicals that easily are converted into \(\text{O}_2\), which do not oxidize as \(\text{OH}^\bullet\) radicals (Laat and Le, 2006). Phenol reacts according to reported reaction pathways (Devlin and Harris, 1984), from which hydroquinone, catechol, p-benzoquinone and o-benzoquinone were identified as main products.

![Graph of phenol conversion vs. Cu²⁺ concentration](image1)

Figure 2. Homogeneous catalytic phenol oxidation at 30°C. Influence of Cu²⁺ concentration at different (Ph/\(\text{H}_2\text{O}_2\)) molar ratio. \([\text{Ph}]_0=1 \text{ g l}^{-1}\). Reaction time=2h.

The conversion of total organic carbon (TOC) of the previous experiments are presented in Figure 3. As it can be seen in the figure, the highest mineralisation obtained with \(\text{H}_2\text{O}_2\) as oxidant agent was 45% at a stoichiometric Ph/\(\text{H}_2\text{O}_2\) molar ratio (1:14) and with 200 mg of Cu²⁺ in solution. The influence of the amount of catalyst is higher for the TOC conversion than for the phenol conversion. On the other hand, the TOC conversion is low because the amount of hydrogen peroxide is not enough to mineralise the reaction intermediates identified above.

![Graph of TOC conversion vs. Cu²⁺ concentration](image2)
3.2 Heterogeneous catalysis

The catalytic activity of the polymer-supported and commercial Cu²⁺ catalysts (Cu-P4VP2%, Cu-P4VP25%, Cu-Chitosan and CuO/γ-Al₂O₃ with 10% of copper content) were tested at 30°C and 85 ml·min⁻¹ of air flow rate and with an initial phenol concentration of 1000 mg·l⁻¹. The Figure 4 presents the results of phenol conversion with the heterogeneous catalysts using air as oxidant. As it can be seen in the figure, the values show that Cu-P4VP25% have the better phenol conversion but is not higher than 10%. Oxidation with Cu-P4VP 2% catalyst presents a conversion of 2.5%, while CuO/γ-Al₂O₃ and Cu-Chitosan, strangely, do not present catalytic activity. The operation conditions, temperature about 30°C and atmospheric pressure are the mean reason of this. At these conditions the oxidation rates are to low to see phenol conversion. The results of phenol conversion are similar than the obtained with homogeneous catalysts. The possibility of phenol adsorption onto the catalysts is low, although adsorption effect must be taken into account at a small degree (Dursun and Kalayci, 2005), so that the heterogeneous catalysis becomes a combined process capable to operate with a catalyst that also performs as support of substrate at low percents. Analysing phenol conversion obtained with Cu-P4VP25% catalyst, the adsorption of phenol occurs when Cu²⁺ is released from the polymer and the same behaviour happens with Cu-P4VP 2%. However, the use of air under reaction conditions, still gives a negligible conversion.

In order to improve phenol conversion, hydrogen peroxide was used as oxidant, as in the homogeneous catalysis. Three catalysts (Cu-P4VP 25%, Cu-P4VP 2% and CuO/γ-Al₂O₃) with different Cu²⁺ content (10, 50, 100 and 200 mg) were tested. The other operation conditions were initial phenol concentration of
1000 mg·l\(^{-1}\), stoichiometric Ph/H\(_2\)O\(_2\) molar ratio, temperature of 30°C and two hours of reaction. The Figure 5 shows the results of phenol conversion at these conditions. As it can be observed in the figure, the catalysts with high Cu\(^{2+}\) content obtained the better phenol conversions. The performances of Cu-P4VP 2% and CuO/γ-Al\(_2\)O\(_3\) are comparable, more of 80% of phenol conversion in the best case, while Cu-P4VP 25% gives a lower phenol conversion in all cases. The difference of phenol conversion observed for 10, 50 or 100 mg of copper is not very high, and as the process is not seen as an end treatment, lower quantities of copper should be used in heterogeneous catalysis. Comparing the results of phenol conversion with those of homogeneous catalysis, it can be observed that the values are more or less equals with 200 mg of copper, but lower for lower amounts of copper. This effect can be explained because a small percent of Cu\(^{2+}\) ions are adsorbed inside the polymer matrix where phenol molecules did not have access, then some Cu\(^{2+}\) ions are not available for the oxidation. Another time, higher phenol conversion should be available with higher amounts of supports catalyst but this is not the mean objective. Finally, the catalytic activity of the polymer-supported-Cu\(^{2+}\) catalysts was probed to be competitive with commercial catalysts like CuO/γ-Al\(_2\)O\(_3\).

The TOC conversion of the previous experiments are presented on Figure 6. CuO/γ-Al\(_2\)O\(_3\) provided the best catalytic results of all the tested catalysts with a TOC conversion more than 20%. The results are equal or lower than the obtained with homogeneous catalysis. Because of the presence of partially oxidised products, TOC conversion is lower than phenol conversion. This can also be confirmed by the difference between phenol conversion and TOC conversion, which gives the selectivity towards carbon dioxide. This selectivity increases as phenol conversion and TOC conversion become closer (Suarez-Ojeda et al., 2005). In our case, the selectivity towards carbon dioxide is low.

Finally, the leaching of copper cations from the catalyst is an important characteristic of the material to take care of because the catalytic deactivation and the growing of the concentration of Cu\(^{2+}\) in solution (Fortuny et al., 1999). The leaching degree, as shown in Figure 7, was obtained from analysing a sample of the substrate after oxidation by an Atomic Absorption analyser in order to know the total copper content on solution. For Cu-P4VP 2% and CuO/γ-Al\(_2\)O\(_3\) catalysts the leaching degrees were high, up to 20 mg·l\(^{-1}\), which are not permissible levels for biological plant treatments. On the other hand, Cu-P4VP 25% provides a maximum value of 5 mg·l\(^{-1}\). Therefore the catalytic activity of Cu-P4VP 25% summed to its low leaching degree represents a potential catalyst for phenol oxidation due to its low released Cu\(^{2+}\) concentration is permissible for pre-treated effluents.
Conclusions

It was demonstrated that phenol oxidation can be performed at soft conditions using polymer-supported-Cu$^{2+}$ catalysts and hydrogen peroxide as oxidant agent. The homogeneous catalytic oxidation of phenol using air as oxidant agent at 30°C and atmospheric pressure showed negligible phenol conversions, even though when the temperature is elevated at 50°C. Phenol conversions increased when H$_2$O$_2$ was the oxidant agent. The results were influenced by initial Cu$^{2+}$ concentration and Ph/ H$_2$O$_2$ molar ratio.

Heterogeneous catalytic oxidation of phenol was performed with tailored polymer-supported-Cu$^{2+}$ catalysts and compared with a commercial CuO/$\gamma$-Al$_2$O$_3$. The better catalytic activity was observed for CuO/$\gamma$-Al$_2$O$_3$ and Cu-P4VP 2%, Cu-P4VP 25% gives lower results. The same behaviour was not observed for the TOC conversion. CuO/$\gamma$-Al$_2$O$_3$ and Cu-P4VP 25% gives the same values for low catalysts amount.

The evaluation of the catalytic leaching showed that Cu-P4VP 25% catalyst provides low leaching values which are favourable due to Cu$^{2+}$ concentration more than 5 mg·l$^{-1}$ would be permissible for a possible post-biological treatment.

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