



Supported Cu(II) polymer catalysts for aqueous phenol oxidation

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ABSTRACT

Supported Cu(II) polymer catalysts were used for the catalytic oxidation of phenol at 30 °C and atmospheric pressure using air and H₂O₂ as oxidants. Heterogenisation of homogeneous Cu(II) catalysts was achieved by adsorption of Cu(II) salts onto polymeric matrices (poly(4-vinylpyridine), Chitosan). The catalytic active sites were represented by Cu(II) ions and showed to conserve their oxidative activity in heterogeneous catalysis as well as in homogeneous systems. The catalytic deactivation was evaluated by quantifying released Cu(II) ions in solution during oxidation, from where Cu–PVP₂₅ showed the best leaching levels no more than 5 mg L⁻¹. Results also indicated that Cu–PVP₂₅ had a catalytic activity (56% of phenol conversion when initial Cu(II) catalytic content was 200 mg L⁻¹_{Reaction}) comparable to that of commercial catalysts (59% of phenol conversion). Finally, the balance between activity and copper leaching was better represented by Cu–PVP₂₅ due to the heterogeneous catalytic activity had 86% performance in the heterogeneous phase, and the rest on the homogeneous phase, while Cu–PVP₂ had 59% and CuO/γ-Al₂O₃ 68%.

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1. Introduction

About 97% of water belongs to the oceans and only 3% is fresh water. Moreover, 0.3% of fresh water is distributed in lakes (87%), swamps (11%) and rivers (2%). Thus, available fresh water sources must be preserved from pollution as there is already a deficit on water [1].

Among the wide variety of water pollutants, phenol and its derivatives have become an important environmental water pollution concern [2]. However most of wastewater from industrial effluents contains compounds or inhibitors poorly degradable, or even toxic. Phenolic compounds are strong bactericide even at mild concentrations, in addition, most of phenol derivatives are contemplated as harmful for human health [3].

Between the large variety of soft cleaning technologies, catalytic wet air oxidation (CWAO) with active carbon allows the use of mild operation conditions [4], enhances the oxidation and requires a lower energy than WAO [5]. On the other hand Fenton-based treatments work at lower pressure and temperature conditions [6], providing a rapid and total destruction of phenolic compounds [7]. Nevertheless, these processes have drawbacks when are operated in continuous and it is necessary to remove the homogeneous catalyst [8].

On the other hand, some studies demonstrated that active metal salts are capable to effectively promote the oxidation of recalcitrant

compounds [9]. Moreover, the catalytic activity of Cu(II) is greatly enhanced when H₂O₂ is the oxidant [10]. In particular, the oxidation using Fenton's like reagent is an attractive treatment method for a large number of hazardous and organic materials [11]. For the heterogeneous systems this is still less clear, being a matter of controversy between an initial adsorption step of the H₂O₂ [12] or the organics [13].

The heterogenisation of homogeneous catalysts by immobilisation improves the easy separation of the catalyst and the simple application on continuous processes [14,15]. Moreover the sorption onto materials of biological origins as synthetic and natural polymers is also recognised as emerging technique [16–19]. For instance, the Chitosan or poly(D-glucosamine), is a new class of potentially inexpensive and environmentally friendly substance that exhibits a high specificity towards metal ions [20].

Polymeric metal complexes are synthesised by adsorption processes using a polymer with a content of donating groups such as amine [21–23]. Chitosan-supported metal complexes are employed as catalysts of industrial processes [24]. Some parameters influence the capacity for adsorbing the metal such as its source, the nature of the metal ion or the solution conditions [25]. However, the cross-linking can also cause a decrease in the reactivity of the polymer, due to a reduction in the diffusion properties [26]. The porosity of the material has a great relevance and limits the adsorption capacity [27].

The poly(4-vinylpyridine) (PVP) is also an attractive polymer for immobilisation of metal ions, because of the strong affinity of pyridyl group to metals and its ability to undergo hydrogen bonding. Analysis of the behaviour of PVP–copper complex show that

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carbonyl bond group is a function of the metal concentration [22]. The enhancement of the thermal properties by the formation of more than one nitrogen–copper bond with the same atom of copper allows high temperature processes that improve mass transport inside the reaction system [23].

This research is devoted to the catalytic oxidation of phenol, at mild conditions, through a heterogeneous Cu(II) onto Chitosan and PVP catalysts in a batch stirred tank reactor. The treatment is not seen as an ultimate treatment but has to provide the demanded biodegradability to be sent to a municipal wastewater treatment process.

2. Methodology

2.1. Materials

Copper sulphate pent hydrated ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (reference 61245), as well as poly(4-vinylpyridine) 2% cross-linked powder, PVP₂ (reference 81391) and poly(4-vinylpyridine) 25% cross-linked beads, PVP₂₅ (reference 81393) were purchased from Sigma–Aldrich. 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 [20] and stored in a solution of NaOH 10% (v/v). The commercial copper catalyst, 20% of CuO supported on $\gamma\text{-Al}_2\text{O}_3$, was provided by Harshaw (reference Cu0803 T1/8). Phenol crystallised (reference 144852) was purchased from Panreac with purity higher than 99%. Catechol 99% (reference 13,5011) and hydroquinone 99% (reference H17902) were provided by Sigma–Aldrich. 1,4-Benzoquinone 98% (reference 12309) and Resorcinol 99% (reference 83600) were purchased from Fluka. Hydrogen peroxide 30% (w/v) (100 vol.) PA (reference 121076.1211) was provided by Panreac. Millipore Milli-Q deionised water was used to prepare all solutions.

2.2. Catalyst preparation

The Cu(II) catalysts were prepared by adsorption of Cu(II) ions onto polymeric materials where $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salt was used as source of Cu(II). The catalyst preparation is based on the immersion of 1 g of the polymeric material (either PVP₂, PVP₂₅, or Chitosan) into 200 mL of Cu(II) solutions. The variation of copper concentrations was monitored after 24 h and analysed by UV–vis spectrophotometer at 800 nm of wavelength in the visible range. The adsorption capacity of Cu(II) onto every support was obtained from the adsorption capacity evaluation, where the variation of Cu(II) before and after adsorption, the volume of the substrate and the weight of the used support were related. Then, the obtained catalysts presented adsorption capacities of PVP₂: 370 mg g⁻¹, PVP₂₅: 290 mg g⁻¹ and Chitosan: 120 mg g⁻¹ representing great amount of active catalytic sites. The full characterisation of these catalysts can be found elsewhere [28].

2.3. Oxidation process

The oxidation tests were conducted at low temperature in a batch stirred tank reactor of 180 mL. Fig. 1 presents the oxidation setup. The initial phenol concentration was always 1 g L⁻¹, the temperature 30 °C and at atmospheric pressure air and hydrogen peroxide were used as oxidants. When air was the oxidant, saturated air was bubbled through the reactor with a flow of 85 mL min⁻¹. 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 the added catalyst for the

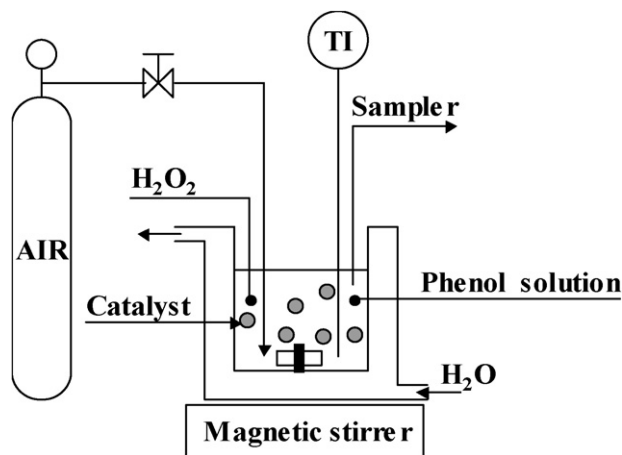


Fig. 1. Catalytic oxidation setup of a batch stirred tank reactor. Heterogeneous catalysis.

homogeneous catalytic oxidation was calculated to provide Cu(II) concentrations of 5, 10, 50 and 200 mg L⁻¹. On the other hand, the amount of added catalyst (W_{CAT}), for the heterogeneous catalytic oxidation, was calculated from a mass balance in the catalyst. It was obtained an equation that related the required amount of Cu(II) at the homogeneous oxidation (W_{Cu}) with the amount of supported Cu(II) onto a specific polymeric material by means of the adsorption capacity (q):

$$W_{\text{CAT}} = W_{\text{Cu}} \cdot \left(1 + \frac{1}{q} \right)$$

The pH was monitored along the reaction time. Reaction progress was monitored by withdrawing 1 mL samples at 5, 20, 40, 60 and 120 min from starting. Then, they were analysed by HPLC to determine the remaining concentration of phenol. Also, the total organic carbon (TOC) at 120 min was determined.

2.4. Analytical procedure

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 at the fifth minute to 1.0 mL min⁻¹ at the seventh minute. 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 took volumes of 20 μL per sample. A calibration curve of phenol was made using aqueous samples of known composition. Intermediates identification was performed by HPLC analyser using aqueous samples of known patterns of each intermediate.

Total organic carbon (TOC) values were obtained by a TOC Analyser (Analytic Jena, model NC 2100). Samples were acidified with 50 mL HCl 2N then were bubbled with synthetic air for 3 min to eliminate the inorganic carbon content and then injected.

Leaching of the catalyst at the end of the oxidation process was determined with an Atomic Absorption Spectrometer (PerkinElmer, model 3110). The analyses were performed at 325 nm with a specific lamp for the element of Cu (PerkinElmer, serial number 01074).

3. Results and discussion

3.1. Homogeneous catalysis

3.1.1. Air as oxidant

Preliminary experiments of phenol oxidation were performed at homogeneous conditions using air as oxidant with a flow of 85 mL min^{-1} . The first attempt was done with a Ph:Cu(II) molar ratio of 1:1, testing two Cu(II) salts (chloride and sulphate) and for the period of 2 h at 30°C . A qualitative evaluation did not show important colour changes promoted by the formation of quinones after the reaction time. The achieved phenol conversion at 30°C was less than 5%, which was not satisfactory at all and the difference between each Cu(II) salt was not significant. So, in order to enhance the reaction performance, the experiments were conducted with a Ph:Cu(II) molar ratio of 1:10 at 50°C for a period of 24 h. The idea of using more severe conditions just reported up to 20% of phenol conversion, although the reaction was not sufficiently improved even with 1:10 molar ratio of Ph:Cu(II). Finally, the conversion obtained after 24 h, 20%, was not acceptable if the purpose is to subsequently send the effluent to a municipal wastewater treatment plant (WWTP). On the other hand the Cu(II) concentration in the reaction solution was too high and it would not be allowed as wastewater influent in any WWTP. Due to the results using air as oxidant were not suitable, it was decided to use a more powerful oxidants as the hydrogen peroxide (H_2O_2).

3.1.2. Hydrogen peroxide as oxidant

The second set of experiments was carried out to evaluate the effect of H_2O_2 . The initial phenol concentration was 1 g L^{-1} , the salt used was $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and the reaction time was 2 h. Three different Ph: H_2O_2 molar ratios were tested (1:1, 1:5 and the stoichiometric 1:14) with four different initial Cu(II) concentrations (5, 10, 50 and 200 mg L^{-1}) at the temperature of 30°C . In this case, the colour of the solution changed, especially at the 20th min where the formation of quinones was evident due to the substrate turned to a dark brown colour, which reflected the formation of phenol intermediates.

Fig. 2 presents the results of phenol conversion using H_2O_2 as oxidant agent after 2 h at the conditions described above. As it can be seen in the figure, phenol conversion increased when Cu(II) concentration was increased and this behaviour occurs for the three molar ratios (1:1, 1:5 and 1:14). It also can be seen that at the equimolar ratio, the phenol conversions were not higher than 50%. Also, at 1:5 Ph: H_2O_2 molar ratio, the phenol conversions were bet-

ter than the equimolar ratio results, presenting conversions from 40 to 85% at different Cu(II) concentrations.

Comparisons between conversions at different molar ratios showed that, phenol conversions achieved at 1:5 Ph: H_2O_2 molar ratio showed a high improvement, almost doubled, compared to conversion at 1:1 Ph: H_2O_2 molar ratio. However, phenol conversions at 1:14 Ph: H_2O_2 molar ratio did not present high increment compared to conversions achieved at 1:5 Ph: H_2O_2 , presenting 1:14 as an approximation of the upper limit of the use of H_2O_2 .

Afterwards, it was expected a proportional increment of phenol conversion when Cu(II) concentration was increased, but the experimental experience showed a different behaviour. From Fig. 2 at 1:1 Ph: H_2O_2 molar ratio it can be seen that phenol conversion had higher increment between 5 and 50 mg L^{-1} than between 50 and 200 mg L^{-1} . This behaviour was also observed at 1:5 molar ratio where phenol conversions increased from 40 to 71% in the range of 5– 50 mg L^{-1} and from 71 to 87% between 50 and 200 mg L^{-1} of Cu(II) concentration. Furthermore, at 1:14 Ph: H_2O_2 molar ratio the phenol conversion follows the same tendency, that is, between 5– 50 mg L^{-1} phenol conversion raised from 44 to 86%, and had a small increase, from 86 to 94%, for the range of 50– 200 mg L^{-1} of Cu(II) concentration. Then, the variation of phenol conversions at different Cu(II) concentrations showed important changes at the first range of 5– 50 mg L^{-1} of Cu(II). Thus, better results were presented at the 50– 200 mg L^{-1} range where phenol conversion was the highest. Afterwards, the Cu(II) load had a positive effect on the conversion, confirming results presented by Aguiar and Ferraz [29]. Even though the high-Cu(II) load could be lowered in order to follow the effluent directives, where there are not permissible higher Cu(II) concentrations than 5 mg L^{-1} [2]. However, the catalytic activity at high-Cu(II) concentrations was hindered due to hydrogen peroxide produced an excess of OH^\bullet radicals that were easily converted into O_2 with a much lower oxidising power [30]. As expected, phenol seemed to react according to reported reaction pathways [31], from which cathecol, hydroquinone, resorcinol and 1,4-benzoquinone were identified as main earlier reaction intermediates.

The conversions of total organic carbon (TOC) of the above tests are shown in Fig. 3. It can be observed in the figure, that TOC conversion increased with the increment either of Ph: H_2O_2 molar ratio, or Cu(II) concentration. At 1:1 Ph: H_2O_2 molar ratio, the mineralisation was low, between 1–6%, compared with the mineralisation achieved at 1:5 Ph: H_2O_2 molar ratio, where the values were between the ranges of 1–32%. This improvement of the mineralisation, in more than four times the value achieved at 1:1

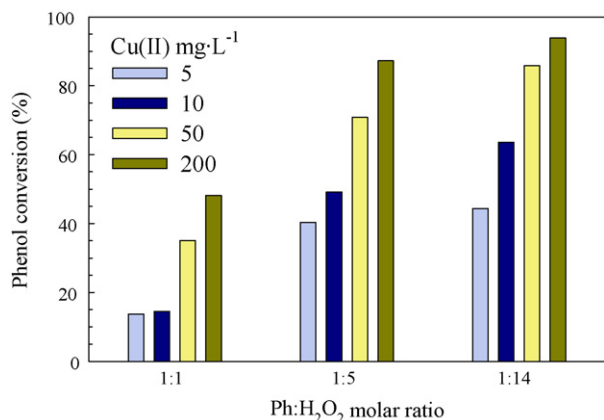


Fig. 2. Homogeneous catalytic phenol oxidation: influence of Cu(II) concentration (mg L^{-1}) at different (Ph: H_2O_2) molar ratio. $[\text{Ph}]_0 = 1 \text{ g L}^{-1}$; reaction time = 2 h; $T = 30^\circ\text{C}$.

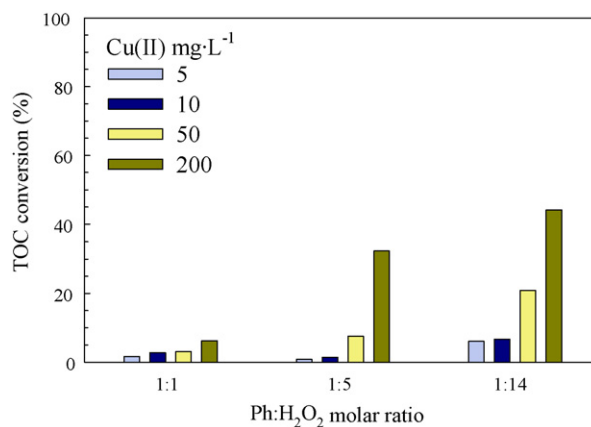


Fig. 3. TOC conversion of homogeneous catalytic phenol oxidation: influence of Cu(II) concentration (mg L^{-1}) at different Ph: H_2O_2 molar ratio. $[\text{Ph}]_0 = 1 \text{ g L}^{-1}$; reaction time = 2 h; $T = 30^\circ\text{C}$.

Ph:H₂O₂ molar ratio, was attributed to the increment of H₂O₂. Moreover, the TOC conversion at 1:14 Ph:H₂O₂ molar ratio was also higher than 1:5 Ph:H₂O₂ molar ratio. This time, the increment was lower than comparison between 1:1 and 1:5 because presenting values were between 6 and 44% of TOC conversion. Additionally, it can be observed that at 1:1 Ph:H₂O₂ molar ratio, the variation of Cu(II) concentration had low influence on the mineralisation of phenol due to the proportion of OH• radicals were low, at this Ph:H₂O₂ molar ratio. At 1:5 Ph:H₂O₂ molar ratio, there was a high improvement of TOC conversion, it was presented between the range of 50–200 mg L⁻¹ of Cu(II) concentration, where TOC values increased from 8 to 32%. Besides, at 1:14 Ph:H₂O₂ molar ratio, TOC conversion also had the highest increment in the range of 50–200 mg L⁻¹ of Cu(II) concentration, which can explain the pseudo stationary behaviour, at this range, presented on the phenol conversion profiles. Thus, comparing phenol and TOC conversion results, it could be understood that at the range of 50–200 mg L⁻¹ of Cu(II) concentration, phenol conversion seemed to have no high differences, while TOC conversion had the highest difference. This effect can be attributed to the amount of Cu(II), because the formation of OH• radicals is the result of the presence of Cu(II) ions, which participate on the H₂O₂ decomposition. Thus, the formation of intermediates during the catalytic oxidation requires more OH• radicals, so that more Cu(II) ions to decompose the H₂O₂. In this way, the decomposition of H₂O₂ is directly associated to the amount of Cu(II) used, then the existence of high amounts of Cu(II) ions on the catalytic oxidation media increases the phenol mineralisation. Overall, the presence of partially oxidised products, TOC conversion was obviously lower than phenol conversion. However, the difference between phenol conversion and TOC conversion gives the selectivity towards carbon dioxide. This selectivity increased as phenol conversion and TOC conversion become closer [32]. Besides, TOC was low because the stoichiometric Ph:H₂O₂ molar ratio was not enough to achieve a total phenol mineralisation and because part of the peroxide was decomposed into O₂.

3.1.3. Kinetics and mechanism

Kinetic analysis was applied to the experimental data for a better understanding of the catalytic process. The operational conditions employed the stoichiometric Ph:H₂O₂ molar ratio at 30 °C and 1 atm of pressure. Then, for this purpose, it was used the integrated rate law to evaluate the oxidation process with three kinetic models: zero, first and second order. Zero order model did not fit well with the experimental data due to the correlation coefficients *R*² were lower than 0.81, suggesting that zero order model is not adequate for this process. For the first and second order models, the experimental data have better fitting to the models, the first order model presented correlation coefficients between 0.99 and 0.97, which compared with the ones obtained for the second order (0.99–0.81), showed that the first order model can account for more than 97% of the experimental data variation, as it is shown in Table 1. It is also noticeable that catalytic oxidation depends of the initial Cu(II) concentration because the efficiency increased with increasing Cu(II) concentration, although the use of high-Cu(II) concentrations needs to be controlled. Therefore,

Table 1
Rate law of first order model for the homogeneous catalytic oxidation of phenol

Rate law	Integrated rate law	[Cu(II)] (mg L ⁻¹)	<i>k</i> (min ⁻¹)	<i>R</i> ²
$-\frac{d[A]}{dt} = k[A]$	$[A] = [A]_0 \cdot e^{-kt}$	5	1.6×10^{-3}	0.9991
		10	4.1×10^{-3}	0.9991
		50	7.3×10^{-3}	0.9991
		200	13.8×10^{-3}	0.9752

Table 2

Catalyst weights used for the heterogeneous catalytic oxidation of phenol

	Air 200 ^a	Hydrogen peroxide			
		10 ^a	50 ^a	100 ^a	200 ^a
Cu–PVP ₂ (mg)	133	6.7	33.3	66.6	133.3
Cu–PVP ₂₅ (mg)	160	8.0	40.0	80.1	160.1
CuO/γ–Al ₂ O ₃ (mg)	180	9.0	45.0	90.0	180.0
Cu–Chitosan (mg)	336	16.8	84.0	168.0	336.0

^a Cu(II) (mg L⁻¹).

according to experimental findings and previous discussion, the following scheme shows a possible mechanism [33].

This mechanism shows the formation of OH• radicals, which promote the oxidation of phenol. Besides, the catalytic oxidation is carried since products like hydroquinone and 1,4-benzoquinone are generated as part of the intermediate compounds.

3.2. Heterogeneous catalysis

3.2.1. Air as oxidant

The catalytic activity of the polymer-supported-Cu(II) and the commercial Cu(II) catalysts CuO/γ–Al₂O₃ were tested on the oxidation of phenol. The initial phenol concentration was 1 g L⁻¹, the air flow rate was 85 mL min⁻¹, the reaction time was 2 h, the used temperature was 30 °C and the amount of employed catalyst *W*_{CAT} is presented in Table 2, where the used Cu(II) concentrations of the homogeneous catalytic systems were taken as a reference.

Fig. 4 displays the results of phenol conversion for the heterogeneous catalysis using air as oxidant. Cu–PVP₂₅ shows a phenol conversion of 20% mostly promoted by the adsorption of phenol onto the catalyst surface. Oxidation with Cu–PVP₂ catalyst presented a conversion even lower (2.5%), while CuO/γ–Al₂O₃ and Cu–Chitosan do not allow neither phenol oxidation nor phenol adsorption at these conditions. So that, the low-oxidising power of the molecular oxygen at 30 °C and 1 atm of pressure could probably explain these poor results. At these conditions, the oxidation rates were too low to see any significant phenol conversion. Then, adsorption effect must be taken into account although the possibility of phenol adsorption onto the catalysts is low [34]. For this reason, in Fig. 5 it is presented the phenol adsorption test of the used polymeric materials without Cu(II) content. Results showed low-adsorption degrees when using 0.5 g of polymeric material, that is the case of PVP₂ (15.8%), which presented the highest phenol adsorption capacity, while PVP₂₅ and Chitosan presented 7 and 0.1%, respectively. In any case, the heterogeneous catalysts should

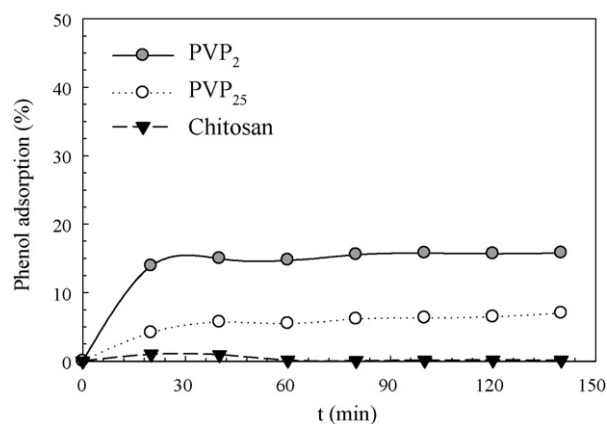


Fig. 4. Adsorption of phenol onto PVP and Chitosan. [Ph]₀ = 1 g L⁻¹; adsorption time = 5 h; *T* = 30 °C; *V* = 180 mL.

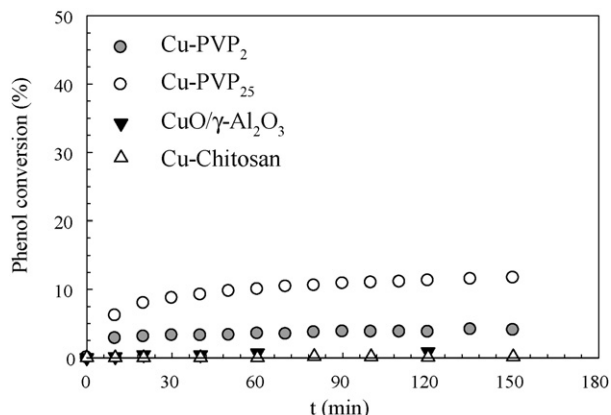


Fig. 5. Heterogeneous catalytic phenol oxidation: comparison between Cu-polymers and a commercial catalyst. Airflow rate = 85 mL min⁻¹; Cu(II) content = 0.05 g; [Ph]₀ = 1 g L⁻¹; T = 30 °C.

be understood in a double way: as the carrier of the Cu(II) ions and as adsorbent due to its ability to adsorb phenol. This last characteristic should enhance the catalytic activity of Cu(II), but when the air is under the present reaction conditions, there is a low possibility of promoting a significant conversion. Consequently it was not difficult to predict a nonexistent TOC conversion because phenol intermediates were not detected by the HPLC.

3.2.2. Hydrogen peroxide as oxidant

In order to improve the phenol conversion, hydrogen peroxide was again used as oxidant. Three catalysts (Cu-PVP₂₅, Cu-PVP₂ and CuO/γ-Al₂O₃) were tested. The amount of each used catalyst is presented in Table 2. At this point Cu-Chitosan was not used due to the structure of the catalyst was easily destroyed in contact with hydrogen peroxide. The other operation conditions were as follows: initial phenol concentration of 1 g L⁻¹, stoichiometric Ph:H₂O₂ molar ratio (1:14), temperature of 30 °C and 2 h of reaction time. Fig. 6 depicts the results of phenol conversion at these conditions. As it can be seen in the figure, the catalysts with the highest Cu(II) content gave phenol conversions between 65 and 80%. From this range, the performance of Cu-PVP₂ with a Cu(II) content of 200 mg L⁻¹ in solution achieved 80% of phenol conversion. Then, the commercial CuO/γ-Al₂O₃ catalyst with an achieved phenol conversion of 87% demonstrated that Cu-PVP₂ can be as good catalyst as a commercial catalyst. On the other hand, Cu-PVP₂₅ achieved

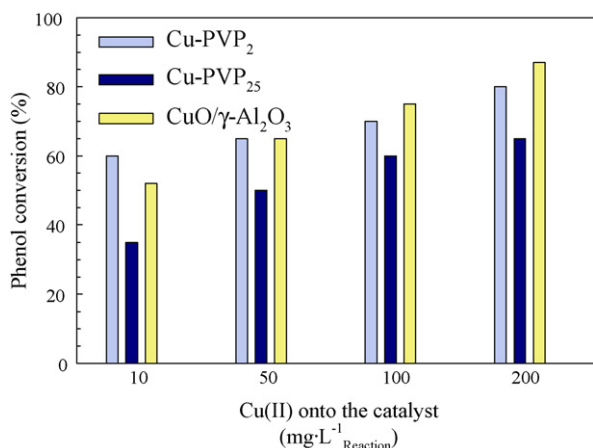


Fig. 6. Heterogeneous catalytic phenol oxidation: influence of initial Cu(II) content. Ph:H₂O₂ 1:14 molar ratio. [Ph]₀ = 1 g L⁻¹; reaction time = 2 h; T = 30 °C.

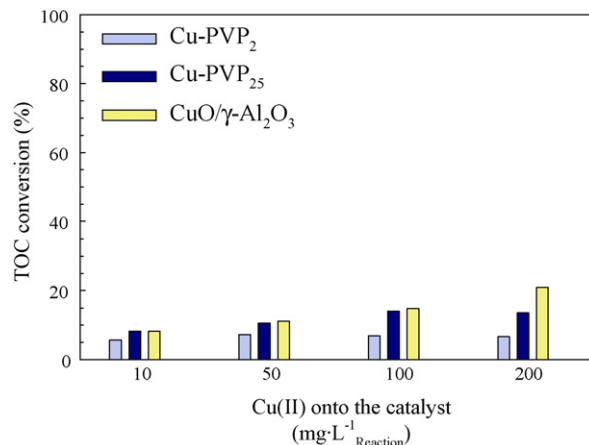


Fig. 7. TOC conversion of heterogeneous catalytic phenol oxidation: influence of the initial Cu(II) content. Ph:H₂O₂ 1:14 molar ratio. [Ph]₀ = 1 g L⁻¹; reaction time = 2 h; T = 30 °C.

65% of phenol conversion on its highest Cu(II) content, presenting much lower conversions at lower amounts of catalyst. Comparing these results with those of homogeneous catalytic oxidation, the conversions were similar at the highest Cu(II) content, but poorer at lower amounts of catalyst. This effect can be explained due to the organisation of these polymeric chains were capable to admit Cu(II) ions between their structures but they were not able to admit the entrance of phenol molecules; as a result, a percent of Cu(II) ions could not participate on the reaction media. Anyway, the catalytic activity of the polymer-supported-Cu(II) catalysts was probed to be competitive with commercial catalysts like CuO/γ-Al₂O₃.

The TOC conversions of the above experiments are presented in Fig. 7. In this figure, CuO/γ-Al₂O₃ provided the best performance of all the tested catalysts, giving a TOC conversion larger than 20% at the highest Cu(II) content. In general terms, the TOC results were equal or somewhat lower than those obtained at homogeneous catalysis. Then, as mentioned on the homogeneous catalytic oxidation, the selectivity towards carbon dioxide was low because of the presence of partially oxidised products, although this effect could not be an inconvenience if these intermediates are biodegradable enough [32].

One thing to take into account is to avoid high levels of catalytic leaching because one of the heterogeneous catalytic aim is to recycle the Cu(II) catalyst. Therefore, it was measured the leaching of the catalyst, which is an important issue promoted by the catalytic deactivation and the increment of Cu(II) content onto the catalyst [4]. In order to know the total copper content in solution, samples of the phenol oxidation reaction were analysed by atomic absorption. Then, the obtained leaching values were graphically presented in Fig. 8, where Cu-PVP₂ and CuO/γ-Al₂O₃ showed a high-copper concentrations in solution after phenol oxidation, up to 20 mg L⁻¹. These leaching levels are not permissible for a subsequent biological plant treatments that allows no more than 5 mg L⁻¹ of copper concentrations. So that, Cu-PVP₂₅ seems to be the better option, between the evaluated catalyst, due to its low-leaching levels are favourable for the process purpose. Then, once it is known the quantities of Cu(II) in solution after oxidation, the catalytic activity can be delimited in homogeneous and heterogeneous phases. So, phenol conversion (*X*) at the real heterogeneous phase (*X_H*) can be calculated by the following relation:

$$X_H = X_T - X_L$$

where *X_T* is the phenol conversion obtained from the experimental catalytic oxidation and *X_L* is the phenol conversion obtained from

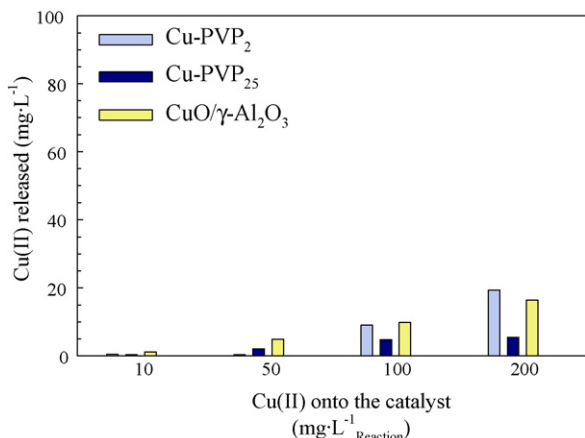


Fig. 8. Leaching of Cu(II) catalyst from heterogeneous catalytic phenol oxidation: influence of the initial Cu(II) content. Ph:H₂O₂ 1:14 molar ratio. [Ph]₀ = 1 g L⁻¹; T = 30 °C.

homogeneous phase and promoted by the leaching of Cu(II). The X_L conversion values were obtained by using Fig. 8, which shows the evolution of phenol conversion at different Cu(II) concentrations in homogeneous phase. Then, X_H conversion values were obtained by using the equation described before, after that, they were presented in Fig. 9. Afterwards, the principle used to separate the phenol conversion of homogeneous and the heterogeneous phase was also applied to the TOC conversion. Thus, in Fig. 10, it can be seen the variation of phenol and TOC conversions under the influence of released Cu(II).

In Fig. 10(a), it is also noticeable that at the increment of Cu(II) content, the percent of homogeneous catalytic activity increased. So that, when using Cu-PVP₂ catalyst with elevated Cu(II) content, phenol and TOC conversions would be highly promoted by the amount of released Cu(II), which would also increase the homogeneous catalytic phenol oxidation. So that, for Cu-PVP₂ case, the maximum phenol conversion, without leaching interference, was 48%.

Fig. 10(b) presents the leaching influence on phenol and TOC conversions when Cu-PVP₂₅ was the catalyst. Phenol conversions augmented in the same way as Cu(II) content on the catalyst was increased. In contrast, TOC conversion increased up to 14% in the range of 10–100 mg L⁻¹ of Cu(II) in solution, but in the last range of 100–200 mg L⁻¹ of Cu(II) in solution, the TOC conversion did not increase as phenol conversion increased at this range. How-

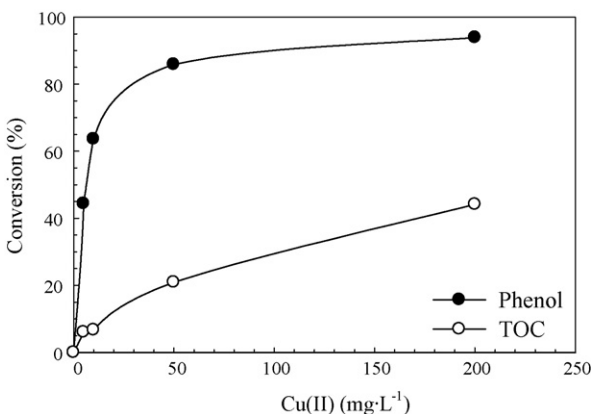


Fig. 9. Homogeneous catalytic oxidation, phenol and TOC tendencies: influence of Cu(II) concentration at Ph:H₂O₂ 1:14 molar ratio. [Ph]₀ = 1 g L⁻¹; reaction time = 2 h; T = 30 °C.

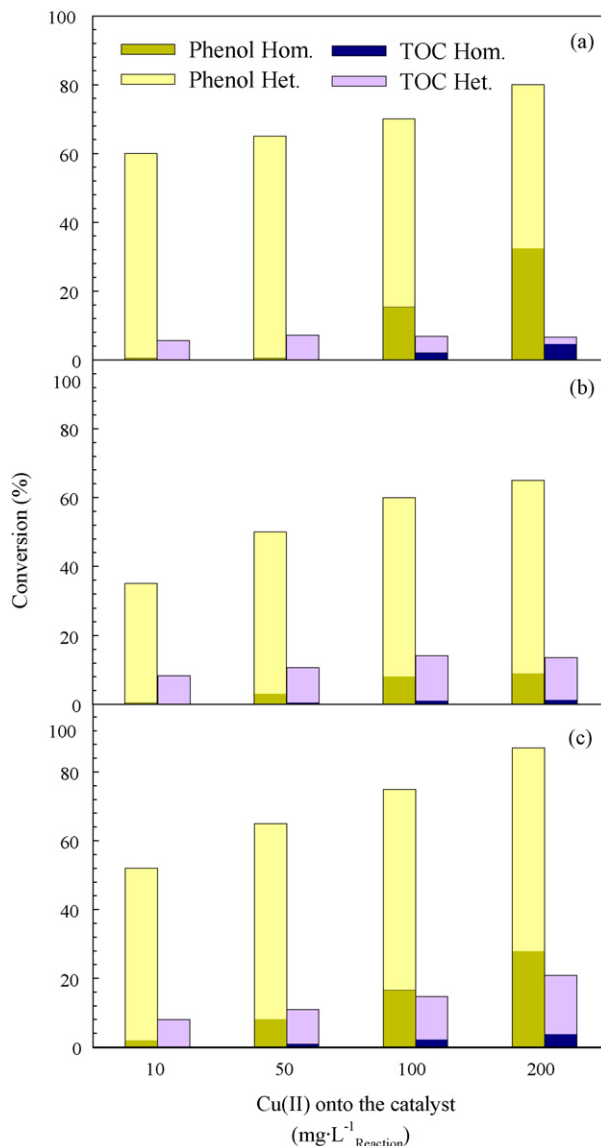


Fig. 10. Phenol and TOC conversions from the heterogeneous catalytic phenol oxidation: influence of the leaching at different initial Cu(II) content. Ph:H₂O₂ 1:14 molar ratio. [Ph]₀ = 1 g L⁻¹; T = 30 °C: (a) Cu-PVP₂, (b) Cu-PVP₂₅; (c) CuO/γ-Al₂O₃.

ever, for Cu-PVP₂₅ case, the leaching degree was not high and the phenol conversion at the heterogeneous phase, without leaching interference, got a satisfactory value of 56%. Thus, the increment of the amount of Cu(II) was beneficial to due it promoted the phenol oxidation avoiding leaching increments.

In Fig. 10(c), it is presented the CuO/γ-Al₂O₃ case, this figure shows the difference between conversions with and without leaching influence and it is noticeable the difference on phenol conversion. Even though phenol conversions were up to 59% without leaching contribution, the leaching of Cu(II) was significant even at low-initial Cu(II) catalyst content. After all, the necessity to increase the amount of catalyst could promote more the homogeneous catalytic activity than the heterogeneous.

Finally, it can be stated from the presented experimental results that the best catalytic oxidation was performed by Cu-PVP₂₅ catalyst due to the 65% of phenol conversion was promoted in more than the 86% by the heterogeneous phase and the 14% was promoted by the leaching.

4. Conclusions

The homogeneous catalytic oxidation of phenol using air as oxidant at 30 °C and atmospheric pressure showed negligible phenol conversions (20%) after 2 h, even when the temperature (50 °C), Cu(II) concentration (1:10 Ph:Cu(II) molar ratio) and time (24 h) were elevated.

Phenol conversion was enhanced when H₂O₂ was the oxidant agent. The results were influenced by the Cu(II) concentration (5, 10, 50 and 200 mg L⁻¹) and the Ph:H₂O₂ molar ratio (1:1, 1:5 and the stoichiometric 1:14).

The heterogeneous catalytic oxidation of phenol using air as oxidant at 30 °C and atmospheric pressure presented low-phenol conversions, up to 12%, after 3 h. There was a possible adsorption stage in spite of an oxidation activity or a combination of both.

Heterogeneous catalytic oxidation of phenol using Cu-polymer catalysts presented the best catalytic activity when Cu-PVP₂ and the commercial CuO/γ-Al₂O₃ catalysts were tested. Cu-PVP₂ showed a phenol conversions of 80% while CuO/γ-Al₂O₃ gave 87%, at the described conditions of 30 °C, atmospheric pressure, 1:14 Ph:H₂O₂ molar ratio and catalysts with the content of 200 mg L⁻¹ of Cu(II) in solution. Although after the leaching evaluation, Cu-PVP₂₅ catalyst, with 65% of phenol conversion, represented the best option because it presented a Cu(II) released up to 5 mg L⁻¹.

Comparison of conversions with and without leaching influence showed that Cu-PVP₂₅ is the best catalytic option due to its leaching levels did not have great influences on the final heterogeneous catalytic oxidation.

Thus, phenol oxidation can be performed at soft conditions using polymer-supported-Cu(II) catalysts and hydrogen peroxide as oxidant agent, although further studies must be conducted to control the catalyst activity, copper leaching and mineralisation degree.

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