Oxidation of Hydroquinone to *p*-Benzoquinone Catalyzed by Cu(II) Supported on Chitosan Flakes

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ABSTRACT: Copper (sorbed on chitosan flakes) was used as a catalyst for the oxidation of hydroquinone, with dioxygen (from air) and hydrogen peroxide as oxidizing agents. The supported catalyst was very efficient at oxidizing hydroquinone into *p*-benzoquinone. With hydrogen peroxide at pH 5.8, drastic oxidizing conditions led to the formation of subproducts. With a short contact time, together with the use of a low hydrogen peroxide concentration and a small amount of the catalyst, the formation of subproducts could be minimized. The influence of the catalyst/substrate and hydrogen peroxide/substrate ratios was investigated to determine optimum experimental conditions for a high initial oxidation rate and a high production of *p*-benzoquinone. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3034–3043, 2006

Key words: catalysis; chitosan; adsorption; selectivity; metal-polymers complexes

INTRODUCTION

Recently, many studies have focused on using chitosan as a support for catalytic reactions. The first applications were directed to enzyme immobilization,[1,2] but during the last decade, much research has focused on the development of chemical catalysts.[3–5] There are several reasons for this interest in using chitosan for supported metal catalysts. This biopolymer has a very high affinity for metal ions.[6] Chitosan is an amino-polysaccharide and is very hydrophilic (because of —OH groups on the glucose unit) and very reactive for metal ions because of the presence of amine groups. These amine groups can sorb metal cations at a nearly neutral pH by chelation (the sorption efficiency decreasing with amine protonation).[7–10] These amine groups also confer unique properties to this material in comparison with other biopolymers. Its pK_a is close to 6.5.[11] In an acidic solution, the protonation of amine groups leads to (1) soluble properties and (2) ion-exchange properties.[12] Metal anions and anionic dyes can be sorbed on chitosan through electrostatic attraction in acidic solutions.[13–17] The dissolution of chitosan in acid media can be prevented by a crosslinking treatment using, for example, glutaraldehyde.[18] This crosslinked material has been used for the sorption of several catalytic metals such as platinum and palladium.[15,19–21] The interaction of chitosan with precious metals has been used to prepare supported catalysts for the hydrogenation of several chemicals such as ketones[22] and chlorophenol and nitrophenol.[23,24] Chitosan has also been used as a support for other metals in such varied reactions as hydrogenation,[25,26] oxidation,[3,27,28] and ring-opening polymerization[29] and the synthesis of fine chemicals.[4,30] Another reason for using chitosan as a support for catalysis is the possibility of conditioning the polymer in very different forms that can open up new avenues for reactor designs. Indeed, chitosan can be prepared in the form of gel beads,[14,18] membranes,[31] fibers,[32] and hollow fibers.[33,34]

This work focuses on the study of an oxidation reaction using copper immobilized on chitosan for the transformation of hydroquinone (HQ) to *p*-benzoquinone (BQ). This reaction was recently investigated by Kucherov et al.,[27] who also used chitosan as the support, and by Owsik and Kolarz,[35] who used a synthetic resin prepared by the grafting of aminoguanidyl groups onto acrylic resins. In their investigation of chitosan as a support for copper and HQ oxidation, Kucherov et al. used two different forms of the copper–chitosan complex: globules of precipitated chitosan complexes and egg-shell bulky particles (binary chitosan–silica gel support). The binary composite system, with a thin film of low-loaded copper–chitosan supported on macroporous SiO$_2$, demonstrated significantly higher ac-

tivity in the oxidation of HQ in comparison with the bulk copper–chitosan sample.

Two different oxidizing agents, dioxygen and hydrogen peroxide, were tested, and the catalyst was used in a powder form. Among the tested parameters were the HQ/copper ratio, the pH, and the concentration of hydrogen peroxide. Special attention was paid to the influence of the experimental conditions on the reaction products because secondary reactions might occur.
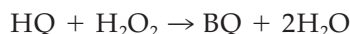
The reaction can be split into two steps:

1. $HQ \rightarrow BQ + 2H^+ + 2e^-$ and
   $2Cu^{2+} + 2e^- \rightarrow 2Cu^+$ or
   $2Cu^{2+} + 2OH^- + 2e^- \rightarrow 2Cu(OH)^+$.
2. $H_2O_2 \rightarrow H_2O + O^*$ and $O^* + 2e^- \rightarrow O^{2-}$ and
   $2Cu^+ \rightarrow 2Cu^{2+} + 2e^-$ or
   $2Cu(OH)^+ \rightarrow 2Cu^{2+} + 2OH^- + 2e^-$.

This results in

1. $HQ + 2Cu^{2+} \rightarrow BQ + 2Cu^+ + 2H^+$.
2. $H_2O_2 + 2Cu^+ \rightarrow H_2O + 2Cu^{2+} + O^{2-}$.

O* represents active molecular oxygen. Assuming that subproducts are not formed, we can write the global reaction as follows:

$$HQ + H_2O_2 \rightarrow BQ + 2H_2O$$

The global rate of the reaction is controlled by the slowest step. Owsik and Kolarz[35] recognized the second step as the rate-controlling step. The reoxidation of the catalytic metal seems to be the limiting step in the process.

The objective of this study was to evaluate the impact of the reaction conditions on the formation of the products (including intermediary or subproducts). An effort was made to correlate these experimental conditions to the formation of byproducts to increase the selectivity of the reaction. The formation of these products was followed with ultraviolet–visible (UV–vis) spectrophotometry with signal treatment facilities that allowed the deconvolution of spectra. In this preliminary work, the study of the stability of the catalyst was not the principal objective. However, the systematic investigation of the effects of selected parameters contributed to identifying the impact of critical parameters such as the concentration of hydrogen peroxide on the stability of the catalytic system.

EXPERIMENTAL

Materials

Chitosan was supplied by Aber Technologies (Plouvien, France). It was characterized by FTIR analysis and size exclusion chromatography (coupled with light scattering and refraction-index measurements) to determine the deacetylation degree (87%) and the molecular weight (125,000 g/mol), respectively.

HQ, BQ, catechol (1,2 benzenediol or *o*-benzoquinone), and resorcinol (1,3-dihydroxybenzene or *m*-benzoquinone) were supplied by Acros Organics France (Noisy-Le-Grand, France), and CuCl_2 was supplied by Fluka France (St Quentin Fallavier, France). Other reagents (acids, sodium hydroxide, and hydrogen peroxide) were supplied by Carlo Erba France (Val de Revil, France). All reagents were analytical-grade products.

Preparation of the catalyst

Chitosan flakes had been previously ground and sieved to collect the 0–125-μm fraction. Chitosan powder (10 g) was dropped into a stirred flask containing 2 L of a CuCl_2 solution at a concentration of 2 g/L. The solution was continuously stirred for 48 h. The copper-loaded material was collected by filtration and dried at 60°C to a constant mass. The concentration was quantified by inductively coupled plasma/atomic emission spectroscopy analysis after the catalyst had been mineralized in an acid solution (in the presence of hydrogen peroxide at a high concentration of 40 vol). The amount of copper in the final product was found to be close to 100 mg of copper/g.

Procedure for catalytic oxidation

One hundred milliliters of an HQ solution at a given concentration was introduced into a dark flask (to prevent photooxidation phenomena). Hydrogen peroxide (when relevant) was added to the flakes before the addition of a given amount of the catalyst. The solution was therefore stirred vigorously (500 rpm) to avoid external diffusion limitations. Some preliminary experiments were performed with dioxygen as the oxidant. In this case, no hydrogen peroxide was added, and the flasks were left open to the air and stirred vigorously (500 rpm) to improve oxygen transfer. The samples were collected and filtered at given contact times for UV–vis spectrophotometry analysis.

Blank experiments were performed in the absence of an oxidizing agent to verify the stability of HQ and to confirm that no significant sorption of the substrate occurred for either the experimental equipment or the catalyst.

Analytical procedures

UV–vis spectra were obtained with an Anthelie Light (Secomam, France) spectrophotometer in the 200–350-nm wavelength range with a Suprasil quartz cell (path length = 10 or 2 mm, scan speed = 1800

nm/min). To identify the different reaction products and evaluate their concentrations in the reaction mixture, a deconvolution procedure was performed with a reference base containing the UV spectra of all the main products that could appear during the reaction on the basis of a literature survey.

The exploitation of the UV spectra was based on a multicomponent approach with the use of a deconvolution method.[36] Any spectrum can be considered a weighted sum of the spectra of absorbing species within the linearity range of the Beer–Lambert law. A classical least-squares algorithm was used to calculate the contribution of the spectra with the study of the associated quadratic error (value and distribution).[37]

In practice, it can be assumed that the UV spectrum (S_w) of an unknown sample can be deconvolved with a linear combination of a small number of defined reference spectra (REF_i) related to either specific compounds or known mixtures (in the compound data base):

$$S_w = \sum_{i=1}^{p} a_i REF_i \pm err$$

where a_i and err are the coefficient of the ith reference spectrum and the deconvolution error, respectively.

The value and distribution of the error are useful for checking the choice of the reference spectra and minimizing the error value. Starting from the previous relation, any additional parameter can be computed with the same linear relation by the replacement of the reference spectra with parameter values.

RESULTS AND DISCUSSION

Oxidation with air: preliminary test of the selectivity of *p*-HQ oxidation

The first experiments were performed with dioxygen in the air. Similar experimental conditions (pH, concentration, amount of catalyst, volume, etc.) were used to compare the oxidation of *o*-HQ, *m*-HQ, and *p*-HQ. A comparison of the spectra clearly showed that the reaction was highly selective of the para position because the spectra of the ortho and meta compounds were not changed, even after 22 h of agitation (Fig. 1). Moreover, this weak variation of the substrate concentration in the solution meant that they were not substantially adsorbed on the catalyst.

The kinetics of HQ oxidation were studied with a larger amount of the catalyst (Fig. 2) in comparison with Figure 1. The first conclusion from this preliminary test was that HQ was only partially transformed into BQ. The transformation increased when the amount of the catalyst was increased. The rate of the transformation was not very high, but the product of
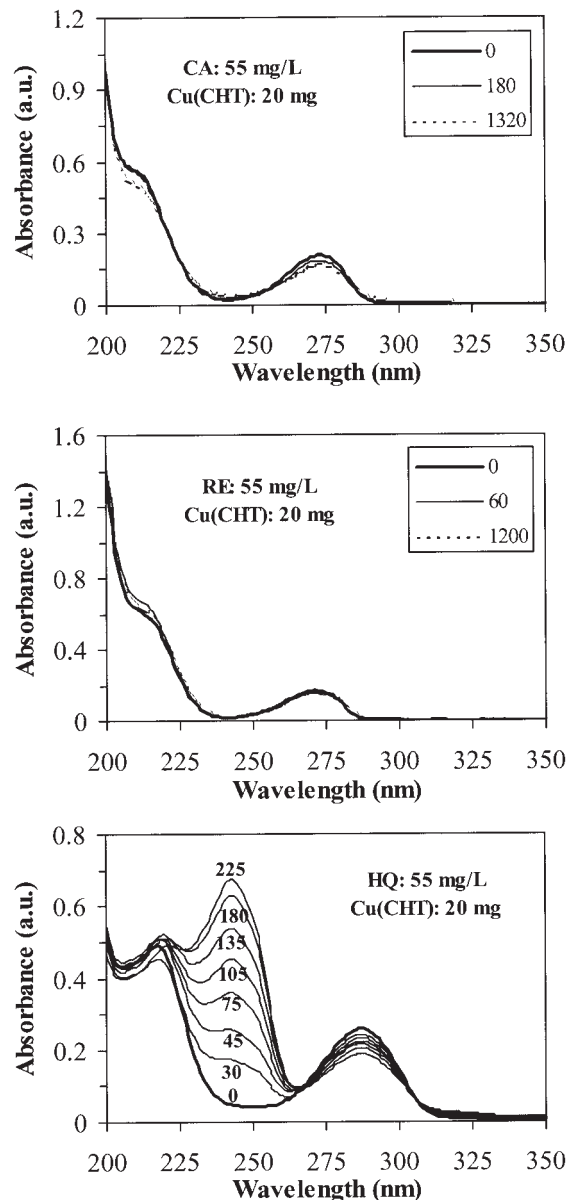

Figure 1 Oxidation of *o*-hydroquinone, *m*-hydroquinone, and *p*-hydroquinone by air, catalyzed by copper immobilized on chitosan flakes (CA = catechol; RE = resorcinol; HQ = *p*-hydroquinone; substrate concentration = 55 mg/L; catalyst concentration = 20 mg in 50 mL). The legend shows the contact time in minutes.

the reaction was only BQ (no additional peak of any UV-absorbing compound other than HQ and BQ), even at a longer contact time (24 h, not shown). The rate of transformation was significantly lower than the levels reached by Owsik and Kolarz,[35] but in their case, hydrogen peroxide was used instead of air. For this reason, in subsequent experiments, hydrogen peroxide was used as the oxidizing agent.

Oxidation of HQ with hydrogen peroxide

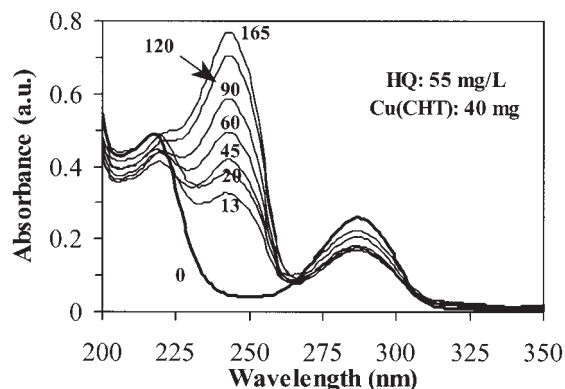Figure 3 (top) shows the UV spectra of the solutions obtained after 1 h of contact of an HQ solution with (1)

Figure 2 Influence of an increasing amount of the catalyst (to 40 mg in 50 mL vs that in the bottom part of Fig. 1) on the oxidation of BQ by the copper catalyst immobilized on chitosan flakes with air as the oxidant (UV spectra at selected contact times).

the catalyst alone, (2) hydrogen peroxide alone, and (3) a combination of hydrogen peroxide with the catalyst. The figure clearly demonstrates that the presence of the catalyst was necessary to achieve a fast and significant transformation of HQ into BQ. However, when the solution was allowed to react for a longer time, the spectrum continued to evolve, and clearly a new product appeared in the solution as a result of a secondary transformation of BQ (Fig. 3, bottom). The absorbance of BQ decreased, and new peaks or shoulders appeared (close to 210 nm), indicating the formation of new compounds, which could be attributed to these byproducts.

Several previous studies focused on the study of HQ oxidation with other systems (other oxidation reactions and other catalysts). Owsik and Kolarz[35] observed that when the concentration of hydrogen peroxide in the solution exceeded a certain value (which depends on the concentration of substrate), the oxidation reaction led to the reoxidation of benzoquinone into 2,5-dihydroxy-*p*-benzoquinone. They observed that in this case a peak appeared in UV spectra at the wavelength 302 nm. This peak did not appear in the present study. Several authors have shown that under very drastic oxidizing conditions, this intermediary product may be transformed into organic acids.[38,39] This may be the case under the experimental conditions selected in this study and could explain the absence of the peak at 302 nm. The most probable reaction path is presented in Figure 4. The comparison of the spectra with those of the possible products of the reaction (according to Fig. 4) showed that the maximum absorbance peak close to 213 nm was very near that of maleic acid (at acid pH) with a peak at 217 nm. However, several shoulders appearing in the spectra of the reaction products confirmed that other intermediary products were also present in the solution.

Figure 5 shows the reference spectra used for the deconvolution procedure (reference base). The variation in the concentration of HQ and BQ together with the variation in the error of the deconvolution operations is shown in Figure 6 for different operating conditions (increasing amount of the catalyst). Although the HQ concentration continuously decreased (with a lowest slope after 60 min of contact), several steps in the variation of the BQ concentration were detected. A first step (during the first 20 min) resulted in a very steep slope for the formation of BQ. This was followed by a lower slope step (from 20 to 50 min). A maximum was reached around 50–60 min, followed by a significant decrease in the BQ concentration. Simultaneously, within the first change in the slope step (after 20 min), *err* increased sharply from less than 0.5 to 2% (at 30 min) and up to 4.5% (at a 2-h contact time). BQ may have been adsorbed onto the support (experiments, not shown, confirmed that low-level adsorption of the reaction product could not be ruled out), but this amount was not consistent with the decrease in the BQ concentration at a long contact time. The change in the spectra and the errors could be clearly
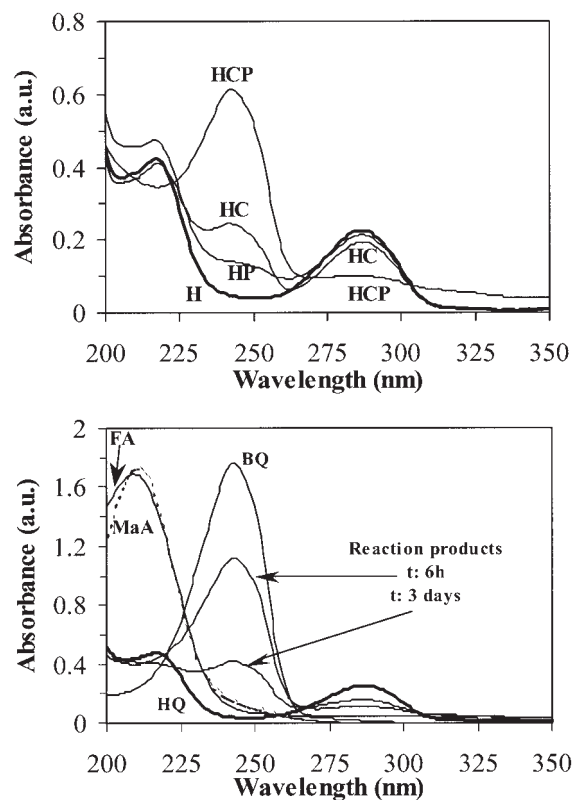

Figure 3 Effect of the oxidation conditions (H = HQ alone; HP = HQ + hydrogen peroxide; HC = HQ + catalyst; HPC = HQ + hydrogen peroxide + catalyst) on the UV spectra of the reaction products after 1 h of contact (top) and spectra of the reaction products (corresponding to HPC conditions) after longer contact times in comparison with HQ, BQ, fumaric acid (FA), and maleic acid (MaA) spectra (bottom).
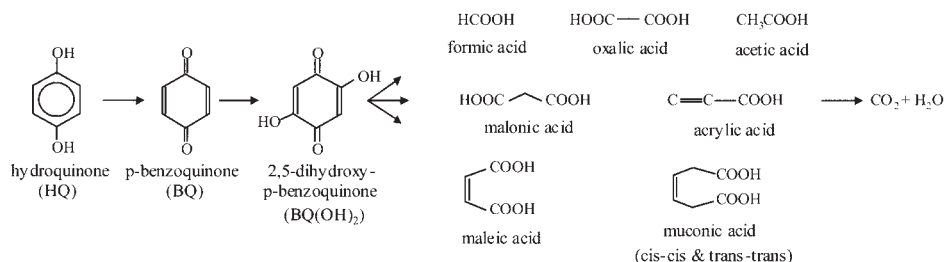
Figure 4   Reaction path for the oxidation of HQ.

explained by the formation of secondary products, in addition to partial oxidation of BQ. Therefore, the strong action of hydrogen peroxide (coupled with the catalyst) resulted in a loss of selectivity and the occurrence of secondary oxidation reactions. Increasing the amount of the catalyst increased the error in the determination of the concentrations, which could be considered accurate only for the first 60 min of contact time (above which the error in the deconvolution of the spectra exceeded 5%).

Complementary experiments were performed with hydrogen peroxide in the presence of BQ (without a catalyst), with no appearance of the new peak being detected at short or long contact times. To avoid too high an excess of hydrogen peroxide causing this secondary reaction, the experiment was performed with successive introductions of very small amounts of hydrogen peroxide at spaced intervals. The same appearance of secondary products was observed (not shown).

pH selection

The oxidation of HQ with hydrogen peroxide is very sensitive to the pH.[35] Some experiments were performed at different pHs without catalyst addition (not shown) and revealed that in alkaline solutions, the oxidation occurred even without the catalyst. The final

product was characterized by a UV spectrum identical to those obtained in the presence of the catalytic system at a lower pH. The reaction was therefore performed at a pH at which the oxidation reaction took place only in the presence of the catalytic material to avoid misinterpretation of kinetic parameters. In an acidic solution, a partial release of copper could occur, and at slightly acid (pH 6) to alkaline pHs, the reaction was autocatalyzed; for this reason, the pH was fixed at pH 5 for further experiments, and the pH was automatically controlled with microadditions of NaOH solutions (with a pH controller from Aquadata, Labo-Moderne, France). There was another reason for using this pH: some experiments were carried out without pH control, the change in the pH was monitored, and the products of the reaction were investigated with UV spectrophotometry. In some cases, the variation in the pH reached 2–3 units in comparison with the initial pH, and a good correlation was observed between the final pH and the type of compound produced at the end of the reaction. Actually, when the final pH was close to 5 (typically 4.7), the spectrum of the final product was very close to that of BQ. On the other hand, when the final pH was lower (less than pH 4), secondary degradation products such as organic compounds were formed (this could also explain the decrease in the pH during the course of the oxidation
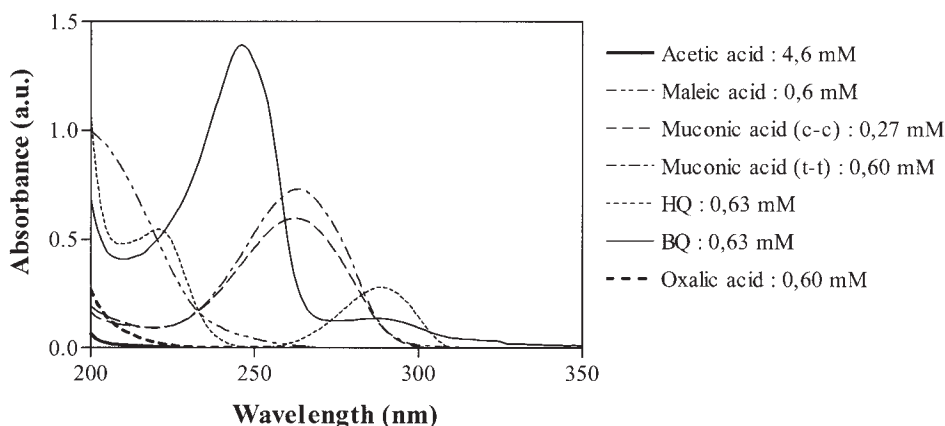

Figure 5   Construction of the reference data base: UV spectra of suspected degradation products.
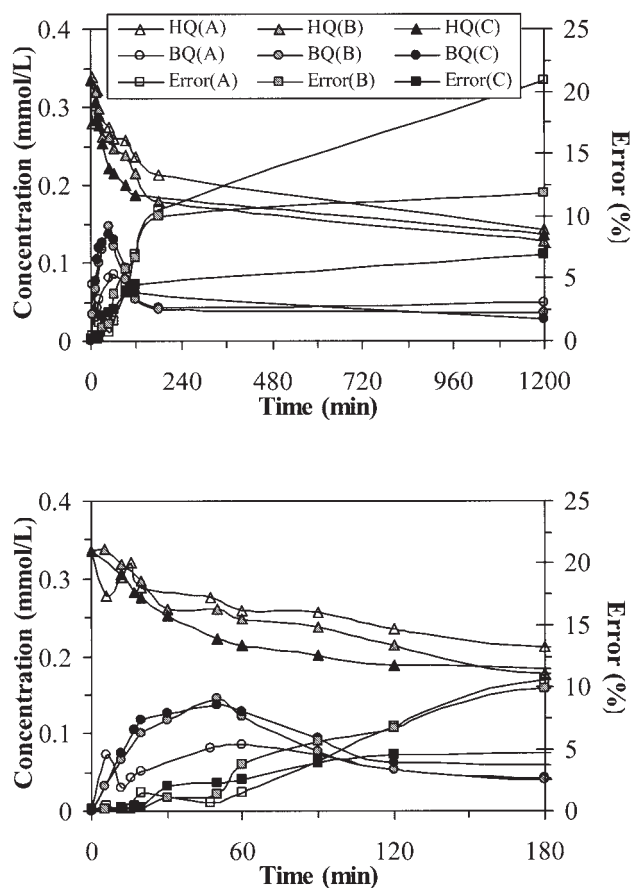
Figure 6 Evaluation of HQ transformation and BQ formation as a function of time by the deconvolution method and evaluation of *r* (the top shows the whole range of contact times, and the bottom shows the initial contact times) for different experimental conditions ([HQ] = 0.8 mmol/L; [H$_2$O$_2$] = 0.8 mmol/L). The catalyst dosage was (A) 5, (B) 10, or (C) 15 mg for 100 mL.

reaction). This is consistent with the findings of Owsik and Kolarz.[35]

The impact of the pH on the reaction kinetics and productivity could also be correlated to the kinetics and thermodynamics of copper reoxidation and to the formation of copper hydroxide complexes. The change in the pH may have caused the formation of copper(II) hydroxide, which could deactivate the catalyst or change the potential to be imposed for metal reoxidation. However, a complementary study (using sophisticated analysis including X-ray photoelectron spectroscopy) would be necessary to confirm this hypothesis.

Influence of the experimental conditions on the oxidation rates and BQ production

In addition to the pH, the experimental design depended on three parameters: (1) the amount of the copper catalyst, (2) the amount of hydrogen peroxide, and (3) the amount of HQ. The experiments were

therefore organized through the variation of the ratios $\alpha = [\text{H}_2\text{O}_2]/[\text{HQ}]$ and $\beta = [\text{Cu(II)}]/[\text{HQ}]$. The concentration of HQ was systematically fixed at 0.63 m*M*. The experimental conditions are more explicitly described in Table I. Samples were collected and analyzed at fixed intervals (3, 5, 8, 10, 15, 20, 30, 45, and 60 min) to monitor the appearance of BQ and its possible degradation. Figure 7 shows the kinetic profile of oxidation reactions for selected experimental conditions (α and β). The initial reaction rate [r_0 (mmol L^{-1} h^{-1})], was determined at 3 min, and the amount of BQ (mmol/L) produced by the reaction was determined at 30 min. This contact time was selected as representative of the BQ formation criterion because it was shown by several experimental series that its concentration reached a maximum at this stage of the reaction. In most cases, BQ production began stabilizing after 30–45 min of contact, whereas the HQ concentration in the solution continued to decrease. This confirmed the fact that secondary products were formed at long contact times. Indeed, depending on the experimental conditions, BQ began to be transformed after 30–45 min: under selected conditions (corresponding to $\beta = 0.2$–0.02 and $\alpha = 3$), the BQ concentration decreased in the solution. An excess of hydrogen peroxide and the catalyst resulted in increased oxidizing power and the formation of secondary products. This is consistent with the conclusions of Owsik and Kolarz.[35] An excess of hydrogen peroxide may also contribute to the degradation of the support and a partial release of copper in the solution, in which the metal can be active as a homogeneous catalyst. Occasionally, an analysis of the solution was performed to evaluate the amount of copper released in the reaction media: this was in most cases less than 10% copper immobilized on the support. In the presence of an excess of hydrogen peroxide (corresponding to $\alpha > 2$), the copper release was increased, showing significant changes in the trend of the curves (Fig. 7). In acidic media, in the presence of large amounts of hydrogen peroxide, chitosan is soluble: this is a degradation procedure that can be used to measure the amount of copper immobilized on the material.

Figure 8 shows the amount of BQ formed after 30 min for each set of experimental conditions. Clearly, the efficiency of BQ production depended on the

TABLE I
Experimental Parameters

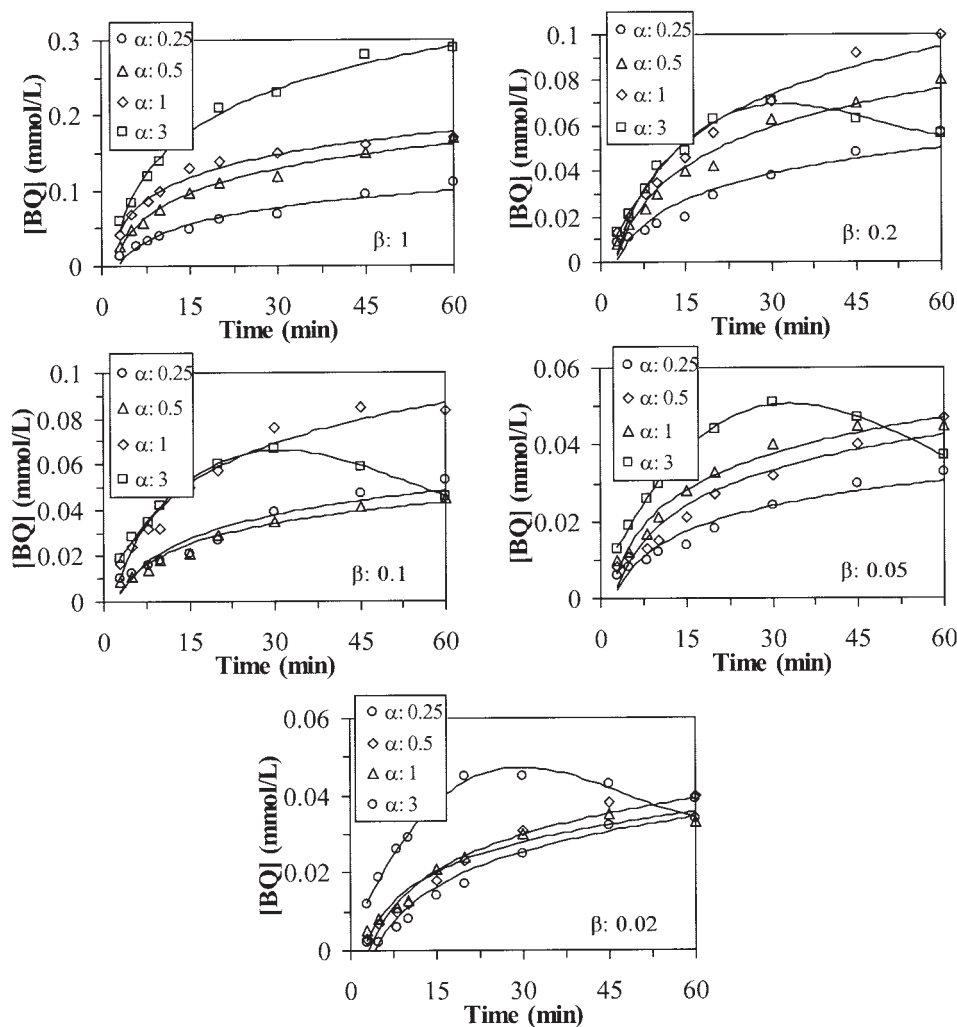|	α			
[H$_2$O$_2$]/[HQ]	0.25	0.50	1.0	3.0
[H$_2$O$_2$] (m*M*)	0.16	0.32	0.63	1.9
	β			
[Cu(II)]/[HQ]	1.0	0.20	0.10	0.050	0.020
[Cu(II)] (m*M*)	0.63	0.13	0.063	0.032	0.013

Figure 7   Kinetics of BQ production as a function of the experimental conditions (α and β) at pH 5.
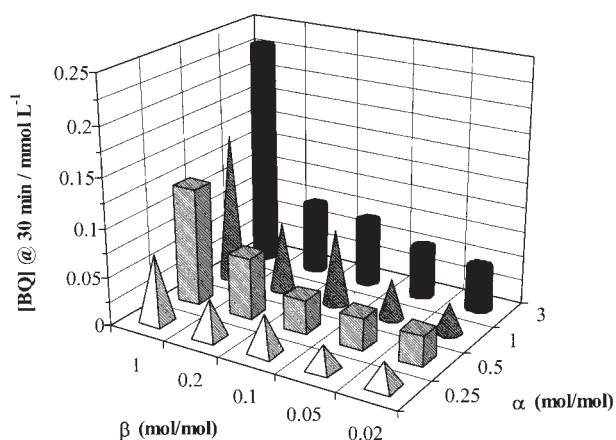

Figure 8   Influence of the experimental conditions (α and β) on BQ production at pH 5, after 30 min of contact, with the copper catalyst immobilized on chitosan flakes.

amounts of both copper and hydrogen peroxide. Increasing the amounts of them in the mixture resulted in a greater production of BQ. However, these parameters did not have a similar effect on the efficiency of the catalytic reaction. Moreover, these experimental factors had a synergistic effect. Increasing the amount of each of them increased the efficiency of the process, but this increase was improved with the simultaneous increase of the second factor. The greatest production was obviously obtained when the concentration of hydrogen peroxide and the amount of the catalyst (copper amount) were maximal within the selected experimental field. However, to optimize the system, it was necessary to maintain a contact time of about 30 min to prevent the formation of secondary products. The initial rates of the conversion are plotted as function of the variations in the experimental conditions (α and β) in Figure 9. Basically, the same trends were observed as in Figure 8. Increasing both the amount of the catalyst and the hydrogen peroxide concentration substantially increased r_0.
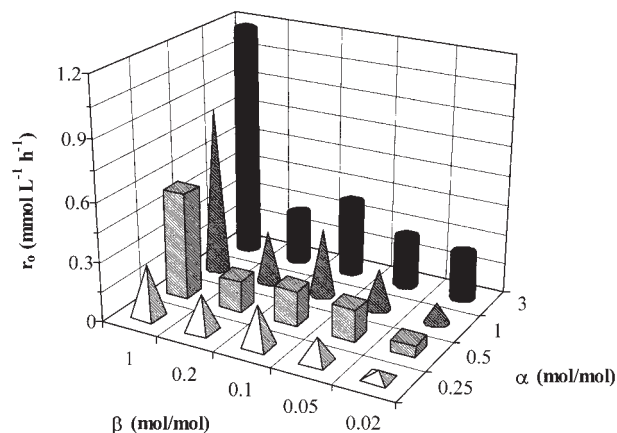
Figure 9 Influence of the experimental conditions (α and β) on the initial conversion rate at pH 5 with the copper catalyst immobilized on chitosan flakes.

The influence of the experimental parameters on BQ production at a contact time of 30 min is presented in Figure 10: BQ production increased almost linearly with the coefficient β, regardless of the value of α (top of the figure). However, increasing α significantly increased the production of BQ. When we consider the variation of BQ as a function of an increasing α ratio (increasing relative hydrogen peroxide concentration), it appears that the effect of the parameter strongly depends on the amount of copper. Although the variation was quite low with small amounts of the copper catalyst, when the β ratio reached 3, increasing the hydrogen peroxide concentration significantly increased the production of BQ, which almost tripled. This is further evidence of the combined effect of the amount of catalyst and hydrogen peroxide concentration. However, the process will have to be optimized, taking into account not only the production of BQ but also the secondary reactions (which reduce the selectivity of HQ oxidation).

Figure 11 shows the effects of the parameters on the initial rate of the reaction. With small amounts of the catalyst, the concentration of hydrogen peroxide hardly influenced the initial rate of the reaction; however, with large amounts of the catalyst, the initial rate of the reaction sharply increased with the concentration of the oxidizing agent.

The kinetics of the reaction can be modeled with the following equation:[40]

$$r = \frac{k_1 C(t)}{1 + k_2 C(t)} \qquad (1)$$

where k_1 (min^{-1}) and k_2 (L/mg) are the kinetic parameters and $C(t)$ is concentration of the substrate at time t. This type of rate law is often observed for heterogeneous reactions in batch reactors with a constant vol-

ume and accounts for reactions that return to the line after the substrate is used. A similar equation (similar to the Michaelis Menten equation) was used to model the effect of the hydrogen peroxide concentration on the initial rate of oxidation. At initial contact times the concentration of hydrogen peroxide can be considered constant (H_2O_2, O). The initial rate of oxidation was plotted as a function of the initial concentration of hydrogen peroxide, and the kinetic parameters were determined after linearization of the equation [plot of r_0^{-1} vs $C(H_2O_2)_2^{-1}$]. Kinetic parameters were determined for each series ($\beta = 1$, 0.2, 0.1, 0.05, or 0.02) for a 0.63 mM concentration of HQ, and the values are summarized in Table II. The influence of HQ was not investigated because the initial amount of HQ was maintained at a fixed value in these experiments, with only the hydrogen peroxide concentration and the amount of the catalyst varied. These values should be taken as indicative values because the quantity of the experimental data was limited for each series (five different concentrations of hydrogen peroxide), and a
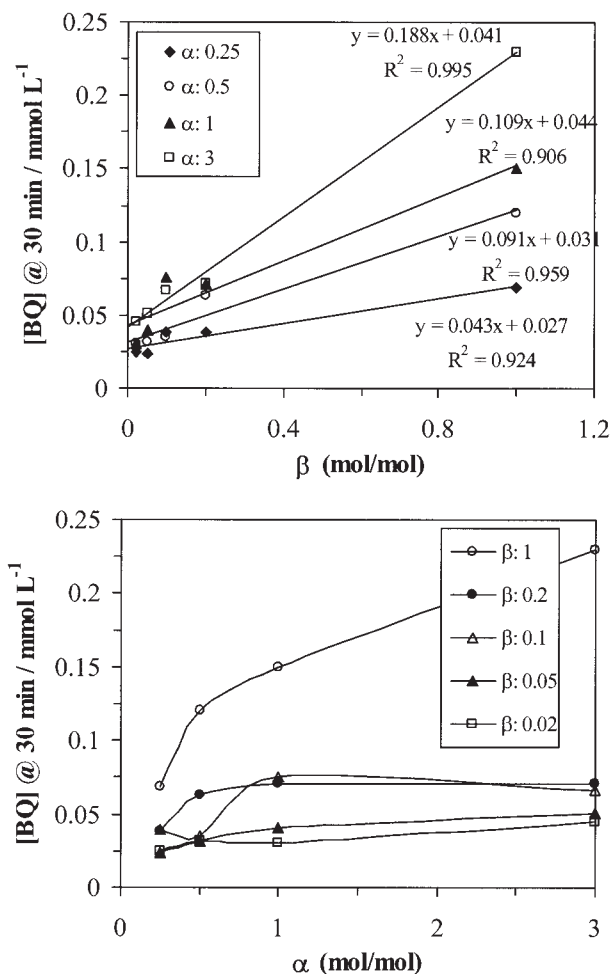

Figure 10 Influence of β on BQ production at 30 min for different α values (top) and influence of α on BQ production at 30 min for different β values (bottom).

significant dispersion was observed in the distribution of the experimental data. However, these data provide information on the trends taking place in the system. The kinetic parameters reached a maximum around a β ratio of 0.2. With larger amounts of the catalyst, the amount of hydrogen peroxide may be insufficient to optimize catalyst activity in the investigated concentration range. It was not possible to increase the concentration of hydrogen peroxide because of the depolymerization of chitosan at high hydrogen peroxide concentrations. The process can therefore be optimized if we take into account (1) the limited hydrogen peroxide concentration suitable for catalyst integrity and (2) the appropriate amount of the catalyst. However, to set these optimum conditions, it is also necessary to take into account secondary reactions that oxidize BQ and contribute to a limitation of the reaction selectivity. Figure 6 shows that an excess of the catalyst contributed to increased synthesis of subproducts.
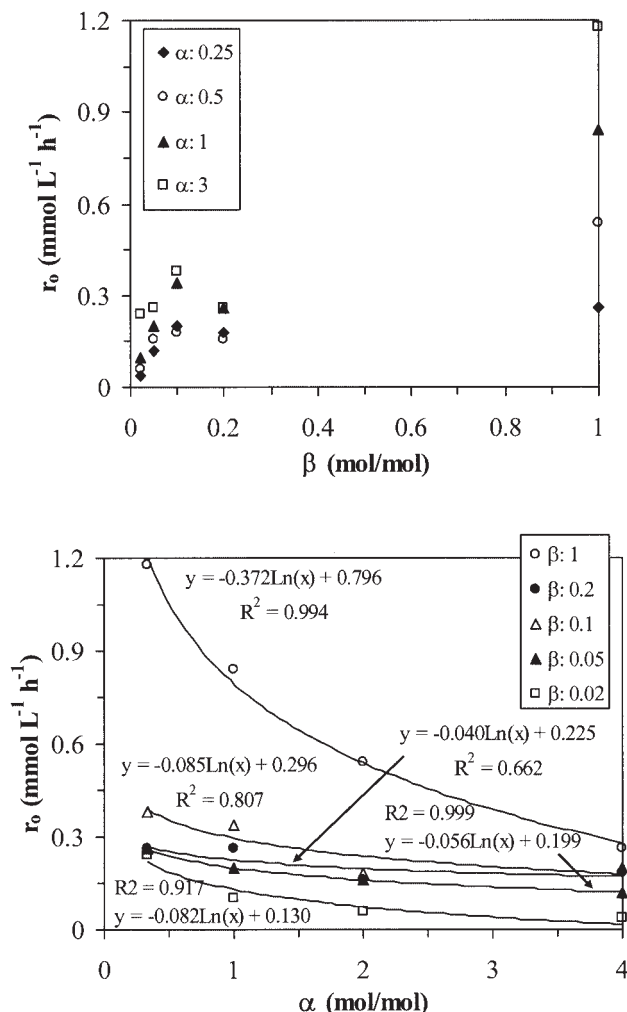

Figure 11 Influence of β on r_0 for different α values (top) and influence of α on r_0 for different β values (bottom).

TABLE II
Kinetic Parameters [in Eq. (1)] for HQ Oxidation: Influence of the Hydrogen Peroxide Concentration at Different β Values

β	$k_1 \cdot 10^3$ (s^{-1})	k_2 (L mmol^{-1})
1	0.54	0.77
0.2	0.87	11.0
0.1	0.67	5.56
0.05	0.36	4.76
0.02	0.08	1.00

CONCLUSIONS

Chitosan has been shown to be an interesting support for the immobilization of copper to prepare an oxidation catalyst. The oxidizing agent has to be carefully selected: dioxygen provides very selective oxidation but low production rates in comparison with hydrogen peroxide. With this drastic oxidizing agent, the kinetics of the oxidation reaction are strongly increased but at the expense of a loss in selectivity (resulting in the synthesis of secondary products). This decrease in selectivity is controlled by the amount of the catalyst and an excess of hydrogen peroxide. The optimization of the process obviously depends on the relative concentrations and amounts of hydrogen peroxide and the catalyst, respectively. These two parameters appear to be dependent. A short contact time of the catalyst with the substrate limits the synthesis of these byproducts.

For these reasons, the use of a hollow chitosan fiber (saturated with copper) seems to be very promising, with dioxygen as the oxidizing agent. The solution could be pumped through the lumen of the fiber, whereas dioxygen is maintained outside of the fiber. The controlled diffusion of dioxygen through the fiber and its reaction at the surface of catalytic metal will provide controlled oxidizing conditions that are expected to be appropriate for selective oxidation of BQ; the use of dioxygen and short contact times will prevent the formation of secondary products.

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