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Catalytic oxidation of phenol by hydrogen peroxide over a pillared clay containing iron. Active species and pH effect

Jean-Michel Tatibouët[a,*], Erwann Guélou[a], and Jeanine Fournier[b]

[a]*Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, Université de Poitiers, Ecole Supérieure d'Ingénieurs de Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers cedex, France*
[b]*Laboratoire de Réactivité de Surface, UMR CNRS 7609, Université Pierre et Marie Curie, 4, place Jussieu, 75252 Paris cedex 05, France*

The study of the catalytic behavior of phenol oxidation by hydrogen peroxide in presence of iron has shown that both heterogeneous and homogeneous catalytic systems behave similarly. For both systems, the reaction has been found sensitive to the pH, the highest phenol conversion and TOC abatement being obtained at a pH value close to 3.7. However, the heterogeneous catalytic system appears to be less sensitive to the pH and more efficient in TOC abatement than the homogeneous one. The measurement of ($OH^{\cdot}$) production by an ESR spin trapping technique using DMPO as trapping agent strongly suggests that the main active species are hydroxyl ($OH^{\cdot}$) and/or hydroperoxyl ($HO_2^{\cdot}$) radicals. The very low amount of iron dissolved by the reaction (less than 2% of the initial content) after more than 350 h of work in a continuous flow reactor is a very promising result to develop a catalytic continuous flow process for industrial wastewater purification.

KEY WORDS: pillared clay; hydrogen peroxide; phenol; pH effect; oxygenated active species; ESR spin trapping; continuous flow reactor

1. Introduction

Numerous wastewater streams containing organic pollutants are generated by many industrial processes, agricultural and domestic activities. Environmental regulations and health quality standards become more and more severe. New strategies have to be found to comply with these regulations: existing processes could be improved or new "clean" technologies could be developed as the use of recycled purified on-site water, for example. But, whatever the solution proposed, a specific treatment of the polluted water will remain necessary.

In the case of toxic and bioresistant pollutants, catalytic wet oxidation processes (CWO) using oxygen (CWAO), ozone, hydrogen peroxide (CWPO) or a combination of them could be useful. The use of a catalyst makes the wet oxidation processes more attractive by achieving high conversion and/or high reaction rates at a lower temperature and pressure [1,2]. Moreover, more recent techniques including SCWO (supercritical wet oxidation) and plasma technologies are also in development for the same purpose [3–5].

Homogeneous catalysts are generally very effective but the catalyst recovery from the effluents requires additional separation operations which increases the cost of the process. Such drawback could be overcome by using stable heterogeneous catalysts.

Among all the possibilities of catalytic wet oxidation processes (depending on the oxidizing agent) the CWPO process using hydrogen peroxide as oxidant was chosen and investigated in our laboratory. Our approach was based on the concept that a catalyst able to be used in the CWPO process should be constituted by a porous support whose role is to adsorb and concentrate the pollutants on its surface, on which sites able to activate hydrogen peroxide are present. In such a way, pillared clays containing iron species could constitute a possible catalyst [6]. In the present paper the results obtained with an Al–Fe pillared clay catalyst used for the phenol oxidation are reported.

Phenol can be considered as a model molecule, representative of the functionalized aromatic molecules class known for their toxicity [7–11]. These molecules are largely present in petrochemical, chemical and pharmaceutical industries wastewater.

As in homogeneous systems where the role of $HO^{\cdot}$ radicals in Fenton like reactions remains still controversial [12], the true nature of the oxidative species in presence of an heterogeneous catalyst is not yet clearly identified since oxygenated radicals ($HO^{\cdot}$, $HOO^{\cdot}$, $O_2^{-\cdot}$) or surface metal-oxygenated species can be proposed as active oxidative species.

Electron spin resonance (ESR) is a highly sensitive technique for detection and characterization of paramagnetic species such as paramagnetic atoms in solid catalysts or species with unpaired electron such as radicals species in aqueous media [13]. If the characterization by ESR of solid heterogeneous catalysts does not present any difficulty, the radical species detection needs to use a spin trapping technique due to their very short life-time in the nanosecond range for hydroxyl radicals $HO^{\cdot}$ in water, for example. The use of a diamagnetic

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*To whom correspondence should be addressed.
E-mail: jean-michel.tatibouet@esip.univ-poitiers.fr

acceptor molecule (no ESR signal) able to react with the radicals to form a more persistent paramagnetic species allows to detect and quantify by ESR the presence of such short-lived radicals [13,14]. 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) was used as the spin trapping agent due to its excellent ability to form an adduct with O centered radicals [13,15–17].

The aim of this paper is to investigate the role of some parameters both on the catalytic behavior and on the oxygenated radicals ($O_2^{-\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet}$) formation in the catalytic phenol oxidation by hydrogen peroxide.

2. Experimental

2.1. Catalyst

The catalyst was an Al–Fe pillared clay prepared by pillaring a commercial Greek bentonite (Zenith N) by mixed Al–Fe species (sample called FAZA) with an atomic ratio Al/Fe equal to 9. The preparation method was described elsewhere [6,18].

The specific surface area was measured according to the BET method by nitrogen adsorption at 77 K.

The d_{001}-spacing was measured by XRD analysis (Siemens D 5000 apparatus).

The iron content of the fresh and used catalysts were determined by chemical analysis at the "Service Central d'Analyse du CNRS", Vernaison, France.

The main characteristics of the catalysts are gathered in table 1. The catalyst is either in a powder form for batch reactor experiments or as an extrudate (1 × 5 mm) for continuous flow reactor experiments.

2.2. Catalytic oxidation of phenol

2.2.1. Batch reactor

The reaction of phenol oxidation was carried out in a thermostated stirred tank Pyrex reactor (250 mL) in isothermal conditions. The temperature of the reactor was controlled by the circulation of a thermal fluid whose temperature is regulated by a cryothermostat.

The reactor was equipped with a pH electrode (Metrohm) to continuously monitor the pH value of the reaction solution. The pH value can be controlled in the pH range from 2 to 5.5 with a precision less than 0.1 pH unity by addition of small amounts of diluted solutions of HNO_3 (0.1 $mol^{-1}L$) or NaOH (0.1 $mol^{-1}L$). The catalyst (0.5–1 g) was put into 100 mL of an aqueous phenol solution ($[phenol] = 5 \cdot 10^{-4}$ $mol^{-1}L$) under continuous stirring, 15 min before the beginning of the hydrogen peroxide addition. The amount of phenol adsorbed on the catalyst before the beginning of the hydrogen peroxide addition was measured as less than 5% of the initial phenol content. The hydrogen peroxide solution ($[H_2O_2] = 0.1$ $mol^{-1}L$) was added continuously to the phenol solution containing the catalyst from a dosimeter (Dosimat 725 Metrohm) with a constant flow rate of 2 $mL^{-1}h$ ($2 \cdot 10^{-4}$ $mol^{-1}h$). The beginning of the hydrogen peroxide addition was taken as the starting time of the reaction (time zero). After 4 h of reaction, the hydrogen peroxide stoichiometric excess (according to the reaction: $C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O$) was only 1.14.

The reaction was performed under an air flow (2 $L^{-1}h$) bubbling directly through the reaction solution to maintain a high level of dissolved oxygen in the reaction medium in order to optimize the catalytic activity [6].

Homogeneous catalytic reaction was performed under the same conditions but by using iron nitrate as catalyst ($[Fe] = 5$ $mg^{-1}L$).

2.3. Recycling continuous flow reactor

A continuous flow reactor was used to allow the determination of the kinetic parameters of the reaction in steady-state conditions. By using a recycling peristaltic pump it is possible to largely increase the flow rate through the catalytic bed in order to avoid some external mass transfer limitations. Moreover, when the recycling ratio is higher than 10, it was shown that, the plug-flow type recycling reactor has the same behavior than a perfectly stirred reactor (CSTR) which is well adapted to the determination of the kinetic constants of the reaction [19].

The reactor is a cylindrical pyrex tube of 20 mm of inner diameter, equipped with a sintered glass support to maintain the catalyst (1–4 g). The total flow of water containing phenol and hydrogen peroxide passing through the reactor (from the bottom to the top) is obtained by the mixture of two different water solutions containing phenol and hydrogen peroxide, delivered by means of 2 dosimeters (Dosimat 725 Metrohm), respectively. The initial concentration of phenol and hydrogen peroxide at the entrance of the reactor is then $5 \cdot 10^{-4}$ $mol^{-1}L$ and 0.01 $mol^{-1}L$, respectively. These

Table 1
Main characteristics of the FAZA catalysts (used catalyst refers to a catalyst used for more than 350 h in the continuous flow recycling reactor)

	BET surface area (m^2 g^{-1})	d_{001}-spacing (Å)	Fe content (wt%)	Pore volume (cm^3 g^{-1})	Mean pore diameter (Å)
Fresh catalyst	180	17.5	3.01	0.24	53
Used catalyst	200	17.0	2.96	0.25	44

concentrations correspond to a stoichiometric excess of hydrogen peroxide of 1.43.

A peristaltic pump (Masterflex C/L 77120-62) allows to maintain a high recycling ratio. As for the batch reactor the pH is continuously monitored and can be adjusted to the desired value by addition of a diluted HNO_3 solution. The temperature of the reactor is controlled by an external circulation of water whose temperature is adjusted by a cryothermostat.

An air flow was passing through the catalyst bed in order (i) to maintain an oxygen saturation of the water solution (ii) to gently move the catalyst particles (extrudate 1 × 5 mm) to allows the gaseous CO_2 formed by the reaction to be efficiently removed from the catalyst bed where large CO_2 bubbles, isolating the catalyst particles from the water, are visible in absence of air flow.

Whatever the reactor the analytical procedure was the same. Small samples of the reaction solution were analyzed by a High Performance Liquid Chromatography (Waters HPLC) equipped with a Aminex HPX-87H (BioRad) column to determine the phenol conversion and the products formed by the reaction. The Total Organic Carbon (TOC) content was measured by a DC 190 Dohrmann TOC meter to evaluate the efficiency of the catalyst toward the complete phenol mineralization.

2.4. *$OH^{\bullet}$ radicals measurement by ESR spectroscopy*

As previously mentioned, the direct recording of $HO^{\bullet}$ radicals by ESR was not possible due to its too short life time. The use of DMPO (5,5-dimethyl-1-pyrroline-1-oxide) which fastly reacts with $HO^{\bullet}$ radicals to form the stable radical adduct DMPO/$HO^{\bullet}$ (half-life = 2.6 h) [13], allows to detect the $HO^{\bullet}$ radicals formation by ESR and then to estimate their concentration by performing a double integration of the ESR signal of the radical adduct DMPO/$HO^{\bullet}$.

The ESR spectra were recorded at 298K on a Bruker ESP-300E spectrometer in the field range 3390–3450 Gauss, at the microwave frequency of 9.25 GHz (X band).

The $HO^{\bullet}$ measurement was performed by contacting a solution of hydrogen peroxide with the catalyst, in presence of DMPO, in concentration conditions close to those used for the catalytic reaction.

The reaction was carried out in a Pyrex reactor (25 mL) at 25 °C, isolated from the day light to avoid photooxidation of the DMPO or superoxide ion formation by photoreduction of the dissolved oxygen [20,21]. The reactor was equipped with a pH electrode to continuously monitor the pH value of the reaction solution. The catalyst (40 mg) was put into 4 mL of bidistilled water under continuous stirring, 5 min before the addition of 2 mL of hydrogen peroxide (0.04 $mol^{-1}L$) and 2 mL of a DMPO solution (0.1 $mol^{-1}L$) prepared by diluting the pure commercial product (Aldrich). The resulting mixture composition was then: catalyst = 0.5 $g^{-1}L$; H_2O_2 = 0.01 $mol^{-1}L$; DMPO = 0.025 $mol^{-1}L$. Addition of DMPO was considered as the starting time (zero time) of the reaction. Samples were taken at 5, 30 and 60 min for immediate ESR analysis. It was generally observed that the ESR signal of the DMPO/$HO^{\bullet}$ adduct remains approximately stable at its maximum level after 30 min of reaction. This stable value will be used to estimate the hydroxyl radical production.

Blank experiments were performed in the same conditions, but without catalyst in order to estimate the spontaneous degradation of hydrogen peroxide. The quantity of $OH^{\bullet}$ radicals produced by the reaction was then calculated by subtracting to the total quantity of $OH^{\bullet}$ radicals measured in presence of the catalyst, the value obtained from the blank experiment.

The experiments were reproduced at least three times in order to estimate a possible error interval.

3. Results and discussion

3.1. *Catalyst characterization by ESR spectroscopy*

The ESR spectra were recorded on a Bruker ESP-300 E spectrometer with the following settings: central field 4000 Gauss, microwave frequency 9.25 GHz (X band), amplitude modulation 10.25 Gauss, time constant 40.96 ms and gain 2×10^3. The ESR spectra were recorded at 77 K under vacuum, after outgassing at room temperature for 1 h.

According to our previous study [22], the FAZA catalyst presents two narrow signals and a broad one, centered at $g \approx 4.3$, 2.1 and 2.5–2.6, respectively. The narrow signal centered at $g \approx 2.1$ was assigned to the presence of isolated iron species belonging to the pillars either in aluminum atoms substitution or as extra-pillar species. These species have been identified as highly active sites for the phenol mineralization.

3.2. *Homogeneous catalytic reaction (batch reactor)*

The catalytic behavior of the homogeneous reaction in presence of 5 $mg^{-1}L$ of dissolved iron is shown in figure 1. An almost total phenol conversion is reached after 180 min of reaction, but the TOC abatement, after a rapid increase in the first 30 min of reaction shows a slower growth to reach only 25% after 4 h of reaction.

3.3. *Heterogeneous catalytic phenol oxidation (batch reactor)*

A typical catalytic reaction is shown on the figure 1. After an induction period, the phenol conversion grows rapidly while the intermediate products (mainly catechol, resorcinol and hydroquinone) appear until the complete phenol conversion was reached in less than 180 min. Simultaneously, the TOC abatement increases with time until it attains a plateau in the 60–70%

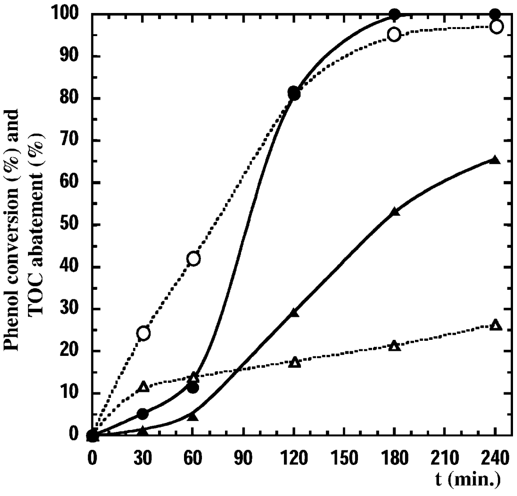

Figure 1. Phenol oxidation by hydrogen peroxide (batch reactor, $T = 25$ °C, $H_2O_2 = 2 \cdot 10^{-4}$ mol^{-1}h, pH = 3.7). Dotted lines and open symbols: homogeneous system ([Fe] = 5 mg^{-1}L) Continuous line and solid symbols: FAZA catalyst = 5 g^{-1}L. (○, ●) phenol conversion; (△, ▲) TOC abatement.

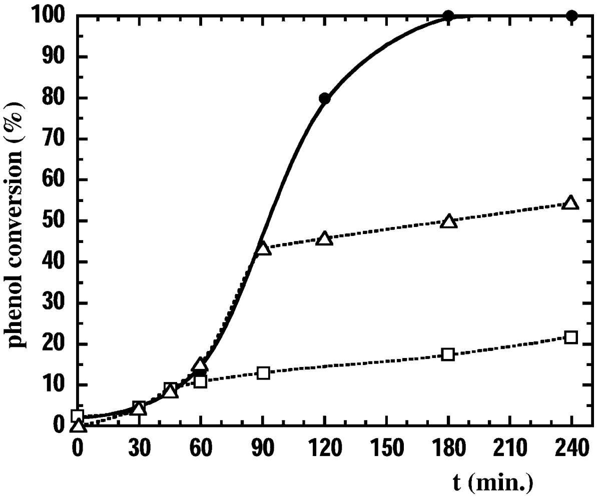

Figure 2. Effect of catalyst removal on the phenol conversion after various reaction times. (batch reactor, $T = 25$ °C, $H_2O_2 = 2 \cdot 10^{-4}$ mol^{-1}h, pH = 3.7, initial catalyst amount = 5 g^{-1}L). (●) catalyst always present; (□) catalyst removed after 45 min of reaction; (△) catalyst removed after 90 min of reaction.

conversion range after more than 4 h of reaction. As already observed with such catalyst [22], a very low leaching of iron occurs (0.2 mg^{-1}L), corresponding to less than 0.15% of the initial iron content in the catalyst. The same catalytic behavior was observed with a reused catalyst showing that the catalyst does not deactivate with time.

In order to test the influence of the homogeneous reaction in presence of a catalyst we have, during a standard experiment, quickly separated the catalyst from the aqueous media by filtration after various reaction times (45 and 90 min) and we have continued the reaction procedure on the filtrated aqueous media. The results (see figure 2) clearly show that after the catalyst removal (but in presence of the lixiviated iron) the phenol conversion does not increase with time. According to this behavior and those observed for homogeneous catalytic reaction by using 5 mg^{-1}L of dissolved iron, we can assume than the homogeneous reaction contribution to the observed phenol conversion and TOC abatement is quite negligible.

3.4. Influence of the pH on the catalytic behavior (batch reactor)

The oxidation reactions were carried out, either in homogeneous conditions with a phenol solution containing 5 mg^{-1}L of iron (from nitrate) or in standard catalytic heterogeneous conditions (catalyst = 5 g^{-1}L) at different pH values from 2 to 4.5. The phenol conversion after 2 h of reaction and the TOC abatement after 4 h of reaction are shown in the figures 3 and 4, respectively.

A broad maximum is observed for the phenol conversion (figure 3), in the pH range 3–3.7 for the homogeneous reaction [23], whereas for the heterogeneous catalytic reaction, a sharp maximum centered for a pH value of 3.7 is observed.

We should notice that the phenol conversion level obtained after 2 h of reaction at pH = 3–3.5 is higher for the homogeneous reaction than for the catalytic heterogeneous one, although the iron content in the reactor for the heterogeneous system was 30 times higher than for the homogeneous one (≈15 mg for the heterogeneous system against 0.5 mg for the

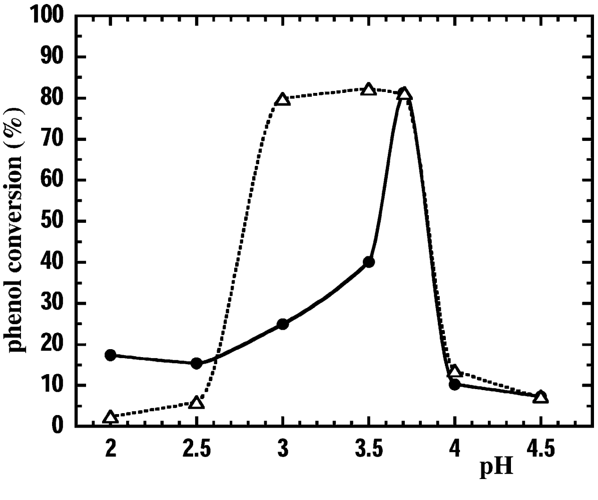

Figure 3. Variation of the phenol conversion in the function of the pH after 2 h of reaction. (batch reactor, $T = 25$ °C, $H_2O_2 = 2 \cdot 10^{-4}$ mol^{-1}h). (△) homogeneous system ([Fe] = 5 mg^{-1}L); (●) heterogeneous catalyst (FAZA = 5 g^{-1}L).

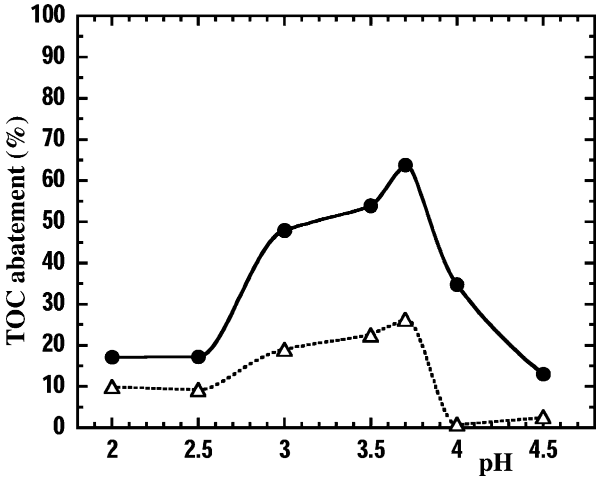

Figure 4. Variation of the TOC abatement in function of the pH, after 4 h of reaction. (batch reactor, $T = 25$ °C, $H_2O_2 = 2 \cdot 10^{-4}$ $mol^{-1}h$). (△) homogeneous system ([Fe] = 5 $mg^{-1}L$); (●) heterogeneous catalyst (FAZA = 5 $g^{-1}L$).

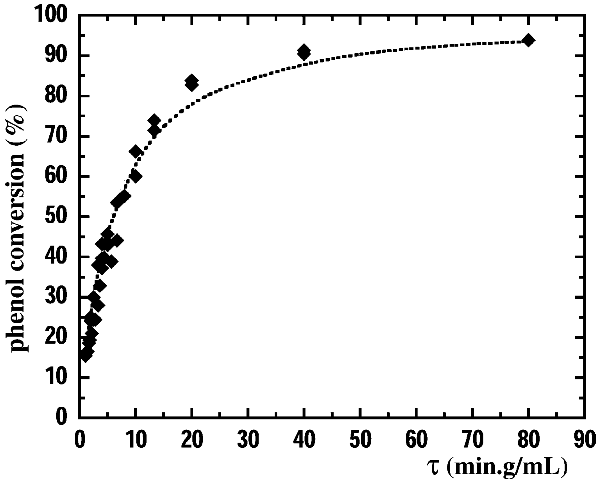

Figure 5. Variation of the phenol conversion in function of the residence time in the recycling continuous flow reactor. ($T = 40$ °C, $[phenol]^{\cdot} = 5.10^{-4}$ $mol^{-1}L$, $[H_2O_2]^{\cdot} = 0.01$ $mol^{-1}L$). Doted line: simulation for $k = 0.18$ mL min^{-1} g^{-1}.

homogeneous one). This observation seems to be due to the induction period observed when an heterogeneous catalyst is used (figure 1). The homogeneous system seems to be very sensitive to the pH values higher than 3, leading to a dramatic decrease in the conversion level, from ≈80% at pH = 3 to less than 5% at pH = 2.5, whereas the heterogeneous system shows only a slight decrease in the phenol conversion from 25 to 17% in the same pH range. The heterogeneous catalytic system appears then to be less sensitive to the pH value than the homogeneous one.

The TOC abatement (figure 4) measured after 4 h of reaction, varies in function of the pH, similarly to the phenol conversion, the TOC abatement value being always higher for the heterogeneous catalyst than for the homogeneous system. However, a clear optimum is also observed for a pH value close to 3.7, for both systems.

3.5. *Continuous flow reactor experiments*

According to the preceding results, all the experiments with this reactor were performed at the optimum pH of 3.7. The recycling ratio was maintained higher than 10 so that the reactor behaves as a perfectly stirred reactor. The variation of the phenol conversion in function of the residence time, which was varied by changing the flow rate and/or the weight of catalyst, is shown on figure 5. The low deviation of the experimental points from the mean experimental phenol conversion curve shows that our reaction kinetic is not limited by external mass transfer phenomena. Moreover, a batch experiment performed by using a catalyst either in extrudate or in powder form has not shown a significant variation in phenol conversion and TOC abatement suggesting that in our conditions internal mass transfer limitations do not occur.

If we assume a one order kinetic reaction for the phenol conversion the rate law for phenol conversion in a perfectly stirred reactor is expressed as it follows:

$$X = k.\tau/(1 + k.\tau)$$

with:

X = phenol conversion

k = rate constant ($mL\,min^{-1}\,g^{-1}$)

τ = catalyst weight/total flow rate ($min\,g^{-1}\,mL^{-1}$)

(The density of our catalyst bed is approximately 1 $g^{-1}mL^{-1}$, so that τ represents also the residence time in min. In this latter case, the rate constant is then expressed in min^{-1}.)
and then:

$$1/X = 1 + 1/k.\tau$$

The rate constant k is then easily determined as the slope of the straight line obtained by drawing $1/X$ in function of $1/\tau$.

The best fit was obtained for a constant k value equal to 0.18 mL min^{-1} g^{-1}, which was used to draw the calculated phenol conversion curve (dotted line) of the figure 5, showing that our simple kinetic model fits very well with the experimental results, especially for a conversion lower than 70%.

Surprisingly, the main intermediate reaction product detected in the effluents exiting the reactor is the oxalic acid, whatever the phenol conversion. The others detected intermediate products in measurable amount are benzoquinones (ortho and para), hydroquinone and catechol (table 2), the benzoquinones formation being unexpectedly higher than those of catechol and hydroquinone for low phenol conversions.

Table 2
Selectivity variation in function of the phenol conversion.
(T = 40 °C, catalyst = 4 g, initial phenol concentration = $5 \cdot 10^{-4}$ mol^{-1}L, initial hydrogen peroxide concentration = 0.01 mol^{-1}L)

Phenol conversion (%)	Benzoquinone (%)	Catechol (%)	Hydroquinone (%)	Oxalic acid (%)
40	8	2	2	25
50	7	4	4	23
60	5	6	1	22
70	4	5	0	24
80	3	4	0	27

These results strongly suggest that the reaction preferentially occurs on the catalyst surface where phenol and intermediate reaction products are strongly adsorbed.

We should also noticed that the FAZA catalyst was highly stable in our reaction conditions since the iron content has been diminished by only 2% of the initial content (table 1), after more than 350 h of use, the catalytic activity remaining almost constant. Moreover, a batch reaction, performed with the same used catalyst has not shown a significant behavior difference with the one observed with a fresh catalyst.

3.6. *Influence of the pH on the hydroxyl radicals production*

The HO$^{\cdot}$production (measured from ESR spectra) in function of the pH value is shown in the figures 6 and 7, for the homogeneous and heterogeneous systems, respectively. A maximum of the hydroxyl radicals production was observed for a pH value around 3.7 for both systems. The same behavior than in the catalytic oxidation reaction is observed for the hydroxyl radicals formation, the heterogeneous catalytic system being less sensitive to the pH value than the homogeneous one.

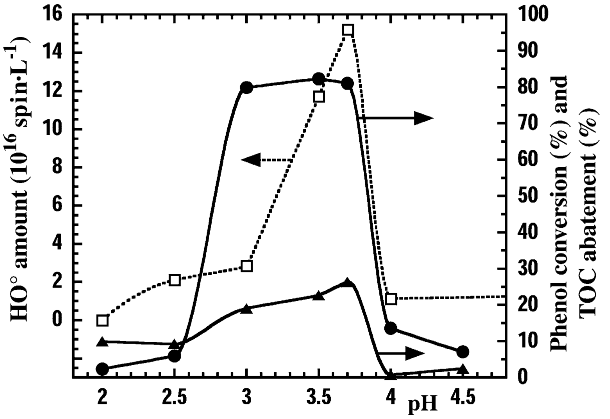

Figure 6. Homogeneous system ([Fe] = 5 mg^{-1}L). Amount of DMPO/HO$^{\cdot}$ adduct, phenol conversion (after 2 h of reaction) and TOC abatement (after 4 h of reaction) in function of the pH. (□) DMPO/HO$^{\cdot}$ adduct amount (dotted line); (●) Phenol conversion; (▲) TOC abatement.

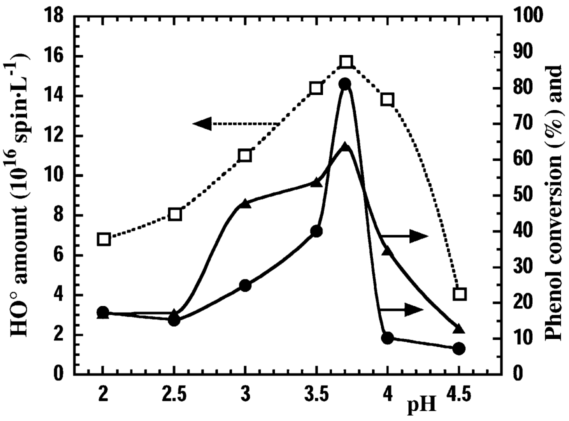

Figure 7. Heterogeneous catalyst (FAZA: 5 g^{-1}L). Amount of DMPO/HO$^{\cdot}$ adduct, phenol conversion (after 2 h of reaction) and TOC abatement (after 4 h of reaction) in function of the pH. (□) DMPO/HO$^{\cdot}$ adduct amount (dotted line); (●) Phenol conversion; (▲) TOC abatement.

According to these results, it is obvious that the pH of the reaction plays an important role in the catalytic activity of phenol oxidation by hydrogen peroxide. A correlation can be done between the amount of DMPO/HO$^{\cdot}$ adduct measured by ESR and the catalytic activity in phenol oxidation (figures 6 and 7). However, the nature of the active oxygen species responsible of this reaction remains questionable since various oxygen species such as HO$^{\cdot}$, $HO_2^{\cdot}$ and $O_2^{-\cdot}$ can lead to the final formation of the DMPO/HO$^{\cdot}$ adduct, directly or after transformation of the initial adduct [13,24].

The DMPO/$HO_2^{\cdot}$ adduct was found highly unstable in aqueous solution, especially in presence of a transition metal [13,24,25], where it is rapidly transformed to DMPO/HO$^{\cdot}$.

The superoxide ion ($O_2^{-\cdot}$) formation could also be possible as in the photooxidation processes [21,25], but at our acidic pH, the superoxide species are rapidly transformed into $HO_2^{\cdot}$ by the following reaction with H^+ [20]:

$$O_2^{-\cdot} + H^+ \rightarrow HO_2^{\cdot} \qquad (3)$$

Moreover, the possible DMPO/$O_2^{-\cdot}$ adduct has a too short half-life (≈60 s) compared to those of DMPO/HO$^{\cdot}$ (≈160 min) [13,24,25] to be detected in our conditions.

From the preceding results, $HO^{\bullet}$ and $HO_2^{\bullet}$ appear then as the more probable active species in our reaction.

According to the Pourbaix diagram of iron species in water [26] it appears that the main species present in our pH study range (2.5–4.5) are $[Fe^{III}(OH)]^{2+}$ and $[Fe^{II}]^{2+}$. The following reactions can then occur in homogeneous or heterogeneous systems:

$$[Fe^{III}(OH)]^{2+} + H_2O_2 \rightarrow [Fe^{II}]^{2+} + HO_2^{\bullet} + H_2O \quad (1)$$

$$[Fe^{II}]^{2+} + H_2O_2 \rightarrow [Fe^{III}(OH)]^{2+} + HO^{\bullet} \quad (2)$$

However, it seems difficult to unambiguously conclude for the heterogeneous system since the catalytic behavior appears to be slightly different to those observed for homogeneous catalytic system. With the heterogeneous catalytic system, the reaction starts after an induction period (not observed for the homogeneous system) and the TOC abatement after 4 h of reaction is largely higher than those observed for the homogeneous reaction. Moreover, some surface species such as iron peroxo or hydroperoxo species can exist and play a role in the catalytic reaction of phenol oxidation.

Nevertheless, according to the similar shape between the $HO^{\bullet}$ production and the catalytic activity, it seems highly probable that the $HO^{\bullet}$ and/or $HO_2^{\bullet}$ species participate in the reaction mechanism. The high TOC abatement observed in presence of the FAZA catalyst which was associated with the presence of the specific iron site identified on this catalyst (isolated iron species belonging to the alumina pillars) clearly shown that the $HO^{\bullet}$ or $HO_2^{\bullet}$ radicals production is not enough to explain all the catalytic behavior observed in the presence of the FAZA catalyst.

The difference between homogeneous and heterogeneous systems could be due either to the formation of different active oxygen from hydrogen peroxide or to the ability of the heterogeneous catalyst to adsorb on its surface the phenol and/or the reaction intermediate products, favoring then their reaction with oxygen species formed by hydrogen peroxide activation. This phenomena could be largely enhanced by the particular structure of the pillared clay where in addition of the adsorbing properties of the pillared clay, the intermediate products of the phenol oxidation could be trapped between the clay layers, favoring then their attack by the oxygenated radicals $HO^{\bullet}$ and $HO_2^{\bullet}$. This behavior could explain the unusual selectivity in oxalic acid formation observed during the continuous flow reactor experiments, the larger molecules than oxalic acid formed by phenol oxidation being trapped inside the clay porosity where they can be easily attacked by $HO^{\bullet}$ and $HO_2^{\bullet}$ species.

4. Conclusion

The study of the catalytic behavior of phenol oxidation by hydrogen peroxide in presence of iron has shown that both heterogeneous and homogeneous catalytic systems behave similarly, the highest phenol conversion and TOC abatement being obtained at a pH value close to 3.7. However, the heterogeneous catalytic system appears to be less sensitive to the pH and more efficient in TOC abatement than the homogeneous one.

The measurement of $OH^{\bullet}$ production by an ESR spin trapping technique using DMPO as trapping agent, has clearly shown that the $OH^{\bullet}$ production followed the same profile in function of the pH value than the catalytic activity in phenol oxidation, strongly suggesting that the main active species are hydroxyl ($OH^{\bullet}$) and/or hydroperoxyl ($HO_2^{\bullet}$) radicals generated by hydrogen peroxide reaction with iron species in homogeneous phase (Fenton reaction) or with iron surface species probably located in the clay porosity.

The very low amount of iron dissolved by the reaction (less than 2% of the initial content) after more than 350 h of work in the continuous flow reactor, is a very promising result to develop a catalytic continuous flow process for industrial wastewater purification.

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