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Comparative study of phenolic compounds mixtures

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Abstract

The photocatalytic degradation of catechol, resorcinol, *m*-cresol, *o*-cresol and phenol has been studied individually, in dual mixtures and in the presence of hydrogen peroxide to determine possible competition for adsorption and photoactive centres and for the radicals photogenerated.

The obtained results have shown that in the presence of hydrogen peroxide degradation rates are determined by the localization of specific adsorption centres more than by the amount of adsorbed molecules or the number of aromatic ring activating positions generated by substituents.

The interaction of catechol with the hydroxyls responsible for the formation of the more photoactive •OH radicals slows down the degradation of the other phenolics.

Additionally, the interaction of each compound with the surface of TiO_2 results in the change of the photoadsorption of oxygen. Consequently, degradation rates of the mixtures are also determined by the photoadsorption of oxygen.

Keywords: Photocatalysis; Mixtures; TiO_2; FTIR; Degradation rate

1. Introduction

The high phenolic wastewater volumes produced by many industrial processes pose a serious environmental threat. Photocatalytic degradation of phenol and its derivatives has been widely studied. In fact, phenol is the most often employed organic for new catalysts characterization [1–15]. It is generally accepted that degradation of these compounds is initiated by the photogenerated •OH attack to the aromatic ring. Therefore, degradation rate has been thought to be determined by the number of activating positions of the ring [16,17]. Also, some authors have proposed a mechanism based on the formation of ozonide-like structures provided by reactions of phenoxy radicals with O_2 or $HO_2^\bullet$ [18–20].

Nevertheless, other important aspects of any catalytic process are:

- the presence of appropriate centers for the adsorption of the organic to be degraded,
- the distance between adsorption and photoactive centers,
- competition between molecules of reagents and/or intermediates for occupying such centers.

As a matter of fact, this last aspect is of paramount importance as aqueous industrial effluents are usually mixtures of different pollutants.

In this work we have studied the photocatalytic degradation of mixtures of phenolic compounds (catechol, resorcinol, *m*-cresol, *o*-cresol and phenol) to determine how the affinity of these organics for adsorption sites affects their degradation. The experiments have been performed at different concentrations (0–100 ppm) to determine if the observed changes are due to the competition for adsorption centres and/or generated radicals or by alteration of the catalyst surface by interaction with the molecules.

The effect of the presence of H_2O_2 and air on the degradation of the phenolic compounds has also been studied to explain the obtained results with the mixtures.

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Nomenclature

r_x	initial degradation rate of the compound x.
$r_{x(y)}$	initial degradation rate of the compound x in the presence of the compound y.
$r_{x(\text{without air})}$	initial degradation rate of the compound x in experiments without air (no bubbling).
$r_{x(N_2)}$	initial degradation rate of the compound x in experiments with nitrogen.
$r_x(H_2O_2)$	initial degradation rate of the compound x in the presence of H_2O_2.
R	resorcinol.
C	catechol.
P	phenol.
o-C	*o*-cresol.
m-C	*m*-cresol.
$[x]_0$	initial concentration of the compound x.
$[x{:}y]_0$	initial concentration of the mixtures of compounds x and y.
$OH^-_{(\cdot OH)}$	hydroxyl groups forming the most photoactive $^\bullet OH$ radicals.

2. Experimental

2.1. Reactions

Aqueous suspensions containing 0–100 ppm of phenol, catechol, resorcinol, *m*-cresol or *o*-cresol and 2 g/L of catalysts (Degussa P-25 TiO_2 powder, 80% anatase and 20% rutile) in 250 mL glass vessels were continuously stirred and air-bubbled (50 mL/min). Additionally, adsorption studies of mixtures (1:1 w:w) of these compounds have been carried out at different concentrations. Though the initial pH of these solutions ranged between 4.5 and 5.5, diluted H_2SO_4 and NaOH diluted solutions were used to set it at 5. Thereafter, it was constantly regulated. Temperature of reactions was always constant at 25 °C. Chemisorption of the organics on the catalyst surface was favoured by bubbling with air and stirring for 30 min before switching on the UV-lamp. Then, the sample was irradiated for 120 min and sampling was performed every 5 min when the initial substrate concentration was lower than 20 ppm and every 15 min if higher ($\geq$25 ppm). Degradation rates were calculated by using the Langmuir–Hinshelwood model [21,22] which provided high regression coefficients (0.989–0.999). In essays with H_2O_2 the concentration of this oxidiser was 50 mM. Adsorption studies were performed in darkness at constant stirring. These experiments lasted also 2 h and samples were taken every 15 min. As in other studies, no adsorption changes were observed after the first 30–45 min [23].

A 60 W Solarium Philips HB175 equipped with four 15-watt Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum at 365 nm) was used as UV source.

2.2. Analysis

The remaining concentrations of the compounds at different reaction times were HPLC-measured using a Macherey-Nagel CC 250/4 NUCLEOSIL 100-5 PROTECT 1 and a acetonitrile–water–acetic acid (40:59.5:0.5) mobile phase, using a UV detector (λ = 270 nm). A FTIR spectrophotometer model RS/1 (UNICAM) was used for spectral analysis. Spectra were obtained in the 1700–1000 cm^{-1} region, employing a resolution of 2 cm^{-1} and a forward and reverse moving mirror speed of 10 and 6.2 kHz. Catalysts were impregnated with (1:5 w/w) phenolic compound-water mixtures and placed between two CaF_2 windows for FTIR measurements.

3. Results and discussion

3.1. Degradation studies of mixtures

Figs. 1–5 show the initial degradation rates of resorcinol, catechol, phenol, *m*-cresol and *o*-cresol, as obtained from individual solutions and 1:1 (w:w) mixtures at different concentrations of the phenolics.

As can be observed in Fig. 1, r_R was progressively increased with $[R]_0$ up to a concentration of 50 ppm. At higher concentrations, r_R was slightly reduced at higher values of $[R]_0$. $r_{m\text{-C}}$ and $r_{o\text{-C}}$ experienced the same behaviour (Figs. 4 and 5). However, r_C (Fig. 2) was much more readily reduced at concentrations over 50 ppm. This is not the case for r_P as it reduction started at concentrations over 75 ppm (Fig. 3).

It has been indicated that formation, migration and reaction of the photogenerated radicals with organic compounds are consecutive reactions. Thus, any of these processes can determine the overall degradation rate. At low concentrations, the reaction of radicals with the organics seems to be the limiting step, and consequently degradation rate increases at higher

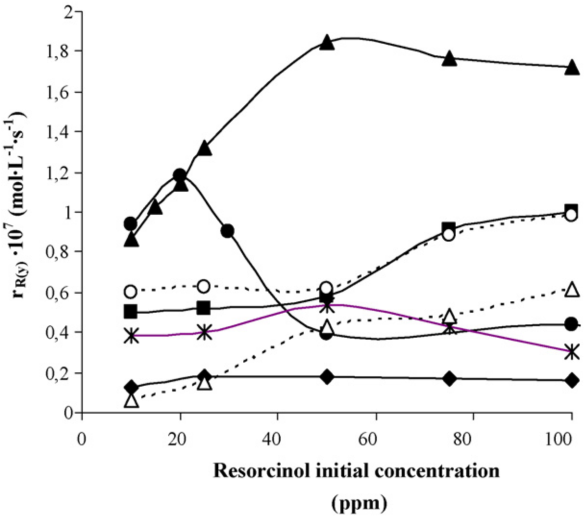


Fig. 1. Initial degradation rate of resorcinol alone (▲, r_R), in mixtures (1:1 w:w) with catechol (◆, $r_{R(C)}$), *m*-cresol (●, $r_{R(m\text{-C})}$), *o*-cresol (Ж, $r_{R(o\text{-C})}$) and phenol (■, $r_{R(P)}$), alone without air (–○–, $r_{R(\text{without air})}$) and under nitrogen atmosphere (–△–, $r_{R(N_2)}$).

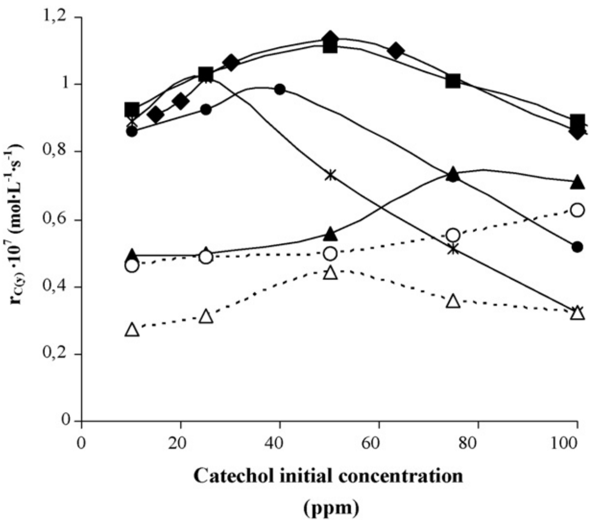


Fig. 2. Initial degradation rate of catechol alone (◆, r_C) and in mixtures (1:1, w:w) with resorcinol (▲, $r_{C(R)}$), m-cresol (●, $r_{C(m\text{-}C)}$), *o*-cresol (Ж, $r_{C(o\text{-}C)}$) and phenol (■, $r_{C(P)}$), alone without air (–○–, $r_{C(\text{without air})}$) and under nitrogen atmosphere (–△–, $r_{C(N_2)}$).

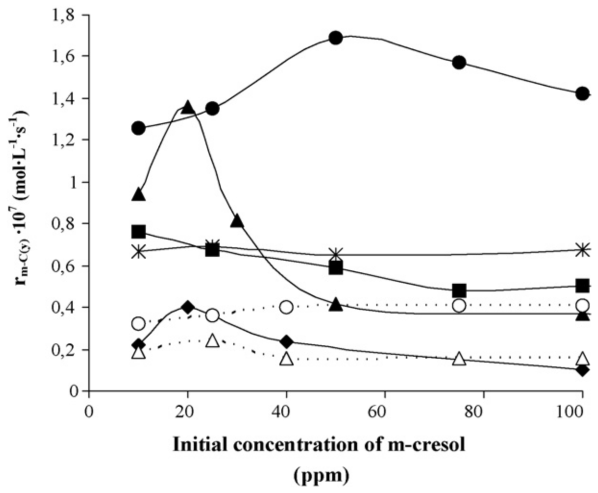


Fig. 4. Initial degradation rates of *m*-cresol alone (●, $r_{m\text{-}C}$) and in mixtures (1:1, w:w) with resorcinol (▲, $r_{m\text{-}C(R)}$), phenol (■, $r_{m\text{-}C(P)}$), *o*-cresol (Ж, $r_{m\text{-}C(o\text{-}C)}$) and catechol (◆, $r_{m\text{-}C(C)}$), alone without air (–○–, $r_{m\text{-}C(\text{without air})}$) and under nitrogen atmosphere (–△–, $r_{m\text{-}C(N_2)}$) are also shown.

initial concentrations. Nonetheless, at high concentrations the formation and migration of radicals can be the determining step. Therefore, the effect of the initial concentration can be the opposite. Intermediates generated during the photocatalytic process can also affect the degradation of parental compounds. Higher initial concentrations of the former will yield higher concentrations of intermediates adsorbed, which can affect the overall degradation rate [24].

In the experiments with the resorcinol-*m*-cresol mixture (Fig. 1), $r_{R(m\text{-}C)}$ started to diminish drastically at an initial concentration of the mixture ([R:-*m*C]$_0$) of 25:25, up to an initial concentration of 50:50. No further modifications were noticed in the other mixtures at higher concentrations. In the studies with the resorcinol: *o*-cresol mixture, $r_{R(o\text{-}C)}$ remained almost unmodified at varying concentrations of the mixture. Additionally, $r_{R(o\text{-}C)}$ was similar to the obtained in the studies in the presence of *m*-cresol at high concentrations, i.e. much lower than r_R. However, in the experiments with catechol and phenol mixtures with the cresols, the obtained $r_{C(m\text{-}C)}$, $r_{C(o\text{-}C)}$, $r_{P(m\text{-}C)}$ and $r_{P(o\text{-}C)}$ diminished progressively, and in some cases remained almost unmodified at concentrations over 25 ppm. This means that cresols seem to be more effective at slowing down the degradation of resorcinol than those of catechol and phenol.

Additionally, the presence of phenol notably reduced degradation rates of resorcinol and the cresols at all the concentrations of the mixtures studied ($r_{R(P)}$, $r_{o\text{-}C(P)}$ and $r_{m\text{-}C(P)}$) (Figs. 1, 4 and 5). Nevertheless, the presence of phenol did not modify catechol degradation rates ($r_{C(P)}$, Fig. 2).

Finally, the presence of catechol in the reaction mixtures resulted in the slowest degradations for resorcinol, the cresols

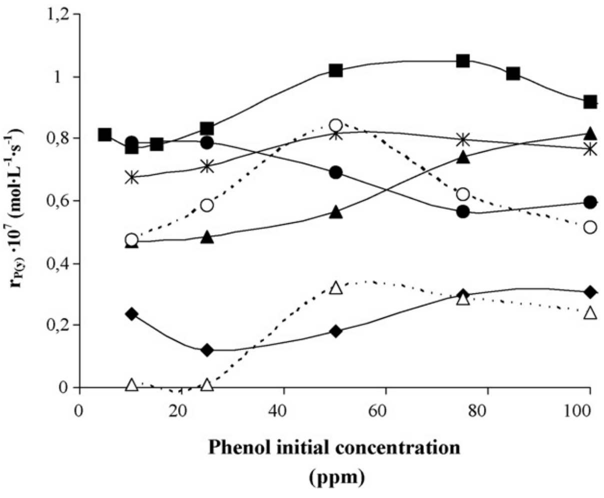


Fig. 3. Initial degradation rate of phenol alone (■, r_P) and in mixtures (1:1, w:w) with resorcinol (▲, $r_{P(R)}$), *m*-cresol (●, $r_{P(m\text{-}C)}$), *o*-cresol (Ж, $r_{P(o\text{-}C)}$) and catechol (◆, $r_{P(C)}$), alone without air (–○–, $r_{P(\text{without air})}$) and under nitrogen atmosphere (–△–,$r_{P(N_2)}$).

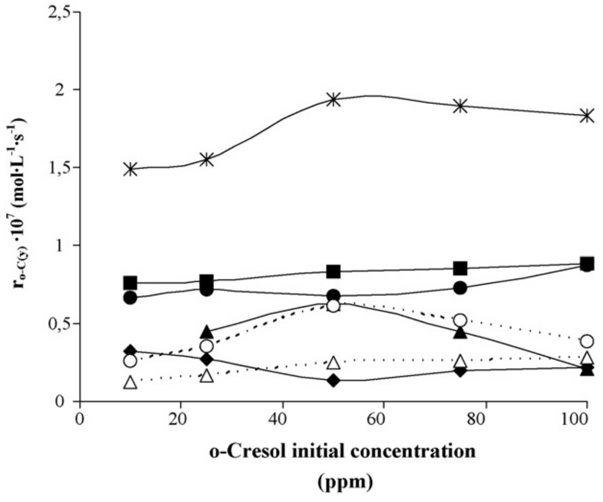


Fig. 5. Initial degradation rates of *o*-cresol alone (Ж, $r_{o\text{-}C}$) and in mixtures (1:1, w:w) with resorcinol (▲, $r_{o\text{-}C(R)}$), phenol (■, $r_{o\text{-}C(P)}$), *m*-cresol (●, $r_{o\text{-}C(m\text{-}C)}$) and catechol (◆, $r_{o\text{-}C(C)}$), alone without air (–○–, $r_{o\text{-}C(\text{without air})}$) and under nitrogen atmosphere (–△–, $r_{o\text{-}C(N_2)}$).

and phenol ($r_{R(C)}$, $r_{o\text{-}C(C)}$, $r_{m\text{-}C(C)}$ and $r_{P(C)}$, respectively (Figs. 1, 3–5).

Additionally, degradation studies without aeration and under nitrogen atmosphere were carried out to evaluate the effect of gaseous and dissolved oxygen in water ($r_{X(\text{without air})}$ and $r_{x(N_2)}$ (Figs. 1–5). Degradation rates of resorcinol, phenol and the cresols without aeration or under nitrogen atmosphere were similar to those obtained with some mixtures. Therefore:

- $r_{R(\text{without air})}$ was very similar to $r_{R(P)}$, and at initial concentrations above 50 ppm $r_{R(N_2)}r_{R(N2)}$ was very similar to $r_{R(m\text{-}C)}$ and $r_{R(o\text{-}C)}$,
- $r_{P(\text{without air})}$ and $r_{P(N2)}$ were intermediate between $r_{P(R)}$ and $r_{P(C)}$,
- $r_{m\text{-}C(\text{without air})}$ was of the same order of $r_{m\text{-}C(P)}$ and $r_{m\text{-}C(o\text{-}C)}$,
- $r_{o\text{-}C(\text{without air})}$ was similar to $r_{o\text{-}C(P)}$, $r_{o\text{-}C(m\text{-}C)}$ and $r_{o\text{-}C(R)}$.

Nonetheless, the lowest catechol degradation rates were obtained without aeration or with nitrogen atmosphere ($r_{C(\text{without-air})}$ and $r_{C(N_2)}$).

The lower degradation rates observed in the mixtures studied could be caused by competition for the photogenerated radicals or adsorption centers.

The photocatalytic degradation of these compounds mainly occurs through $^{\bullet}OH$ radical attack. Hence, to explain the observed differences among their photocatalytic behaviours, the effect of H_2O_2 was studied.

3.2. Degradation studies in the presence of H_2O_2

This oxidiser can speed up the process by providing $^{\bullet}OH$ radicals by means of the following reaction [25]:

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \qquad (1)$$

In the experiments with H_2O_2, air and at concentration lower than 75 ppm (Fig. 6), $r_C(H_2O_2)$ was slightly higher than $r_R(H_2O_2)$ and notably higher than $r_P(H_2O_2)$, $r_{m\text{-}C}(H_2O_2)$ and $r_{o\text{-}C}(H_2O_2)$. Nonetheless, at increased concentrations, catechol and resorcinol degradation rates were quite similar.

However, in the experiments with H_2O_2 but without air and at concentrations above 50 ppm, $r_R(H_2O_2$, without air), $r_P(H_2O_2$, without air) $r_{m\text{-}C}(H_2O_2$, without air) and $r_{o\text{-}C}(H_2O_2$, without air) were higher than those obtained in the presence of air, while $r_C(H_2O_2$, without air) remained almost unaltered. Contrary to this, at lower concentrations the behaviour was the opposite, i.e., $r_C(H_2O_2$, without air) was remarkably increased, while the augmentation of rates of the other compounds was not as significant.

If as indicated by several authors [26–28], the adsorption centers of H_2O_2 coincide with those where radicals are generated, the effect of the oxidiser can be inhibited by means of the reaction:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2{}^{\bullet} \qquad (2)$$

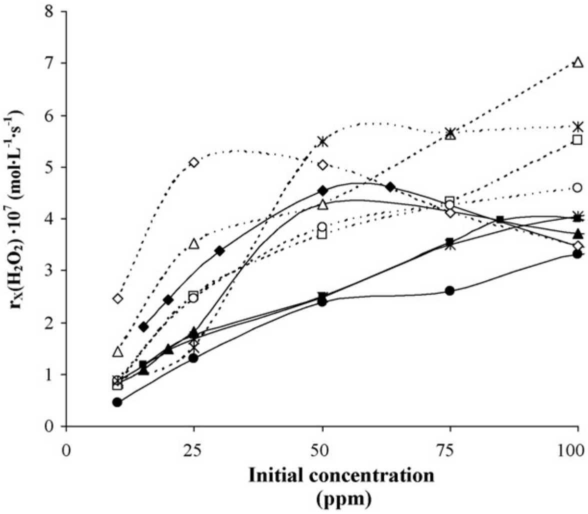


Fig. 6. Initial degradation rates of the different compounds with H_2O_2 (solid symbols and continuous line) and without air + H_2O_2 (empty symbols and discontinuous line) (◆, $r_C(H_2O_2)$, ◇ $r_{C(H_2O_2\text{-without air})}$), (▲, $r_R(H_2O_2)$, △, $r_{R(H_2O_2\text{-without air})}$) (■, $r_P(H_2O_2)$, □,$r_{P(H_2O_2\text{-without air})}$) (●, $r_{m\text{-}C}(H_2O_2)$, ○ $r_{m\text{-}C(H_2O_2\text{-without air})}$) (Ж, $r_{o\text{-}C}(H_2O_2)$, –Ж– $r_{C(H_2O_2\text{-without air})}$).

In addition to this, it has been indicated [26–28] that the hydroxyl groups responsible for the formation of $^{\bullet}OH$ radicals can be regenerated through the reaction of $O_2{}^{\bullet-}$ radicals with acid hydroxyls by means of the reaction illustrated in Scheme 1:

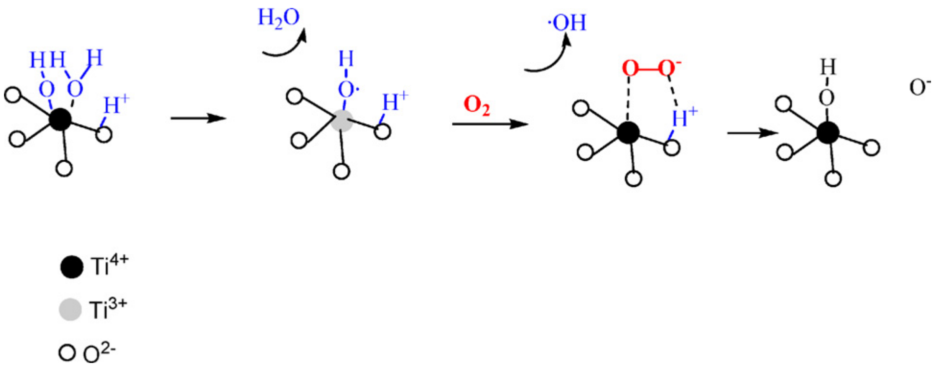
In this way, in the experiments with H_2O_2 + air, the hydroxyls responsible for the formation of the radicals which inhibit the effect of this oxidiser (reaction (2)) are regenerated to slow down degradation. However, without air these hydroxyls are not regenerated and degradation rate is increased. This is what apparently happens in the studies in the presence of H_2O_2 and concentrations above 50 ppm of resorcinol, phenol and the cresols. At lower concentrations the number of hydroxyls responsible for the formation of $^{\bullet}OH$ radicals must be high enough to prevent their complete consumption. This would explain why the effect of air was not so significant.

Nevertheless, the results from catechol + H_2O_2 suggest a completely different behaviour.

3.3. Adsorption studies

As indicated above, another argument to explain the different behaviour of the mixtures is the affinity of the organics for adsorption centres. To check this possibility, individual adsorption studies and with the mixtures have been performed (Fig. 7a–d). As results for *m*-cresol and *o*-cresol in individual and mixture experiments were quite similar, they were not included in the figures.

In the individual experiments, the adsorptions of catechol and phenol on TiO_2 surface were clearly higher than those of the other organics. At concentrations of catechol over 50 ppm, its adsorption was slightly reduced in the presence of the other compounds. However, the adsorption of phenol was strongly affected by the presence of the other phenolics. This was not the case for resorcinol and the cresols, for which no effect of the other compounds was observed.



Scheme 1.

From these results, it can be concluded that the observed changes in degradation rates cannot be attributed to competition for adsorption centers.

3.4. FTIR studies

The tendency of the studied compounds to react with the photogenerated radicals is determined by the ability of their substituents at generating aromatic ring activating positions for radical attack. Several authors claim that the fastest degradations are provided by the more intense activating positions [16,17]. However, the intensity of activating positions can be modified by the interaction of the molecules with the catalyst surface. Consequently, FTIR experiments were conducted to determine the ability of the substituents of the studied compounds at generating activating positions and its effect on photocatalytic activity.

Fig. 8a–e show FTIR spectra from interactions of catechol, resorcinol, *o*-cresol, *m*-cresol and phenol with the surface of TiO_2, between 1800–1000 cm^{-1}.

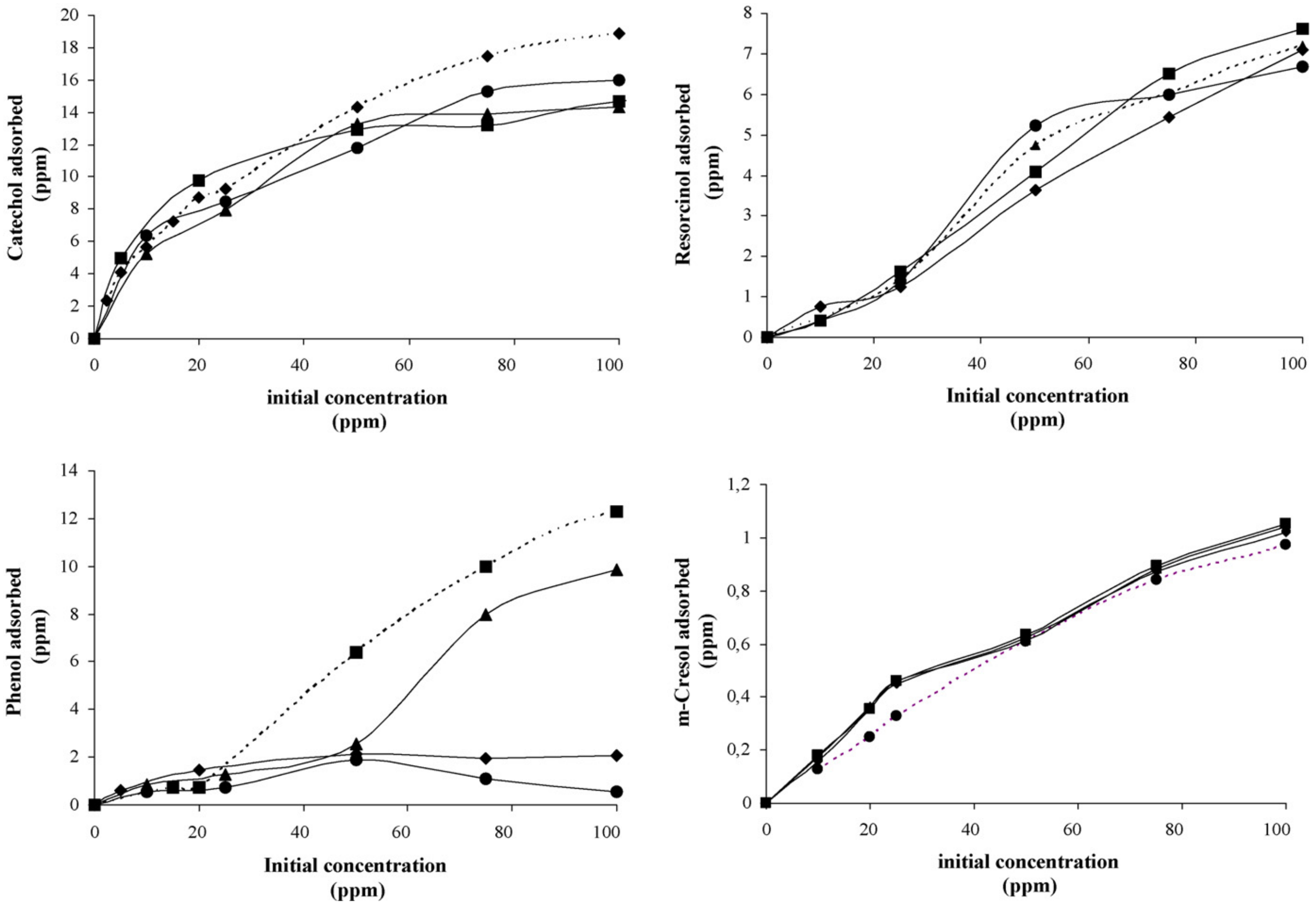


Fig. 7. (a) Adsorption of catechol on TiO_2 alone (◆) and in the presence of resorcinol (▲) or phenol (■) or *m*-cresol (●). (b) Adsorption of resorcinol on TiO_2 alone (▲) and in the presence of catechol (◆) or phenol (■) or *m*-cresol (●). (c) Adsorption of phenol on TiO_2 alone (■) and in the presence of catechol (◆) or resorcinol (▲) or m-cresol (●). (d) Adsorption of *m*-cresol on TiO_2 alone (●) and in the presence of catechol (◆) or resorcinol (▲) or phenol (■).

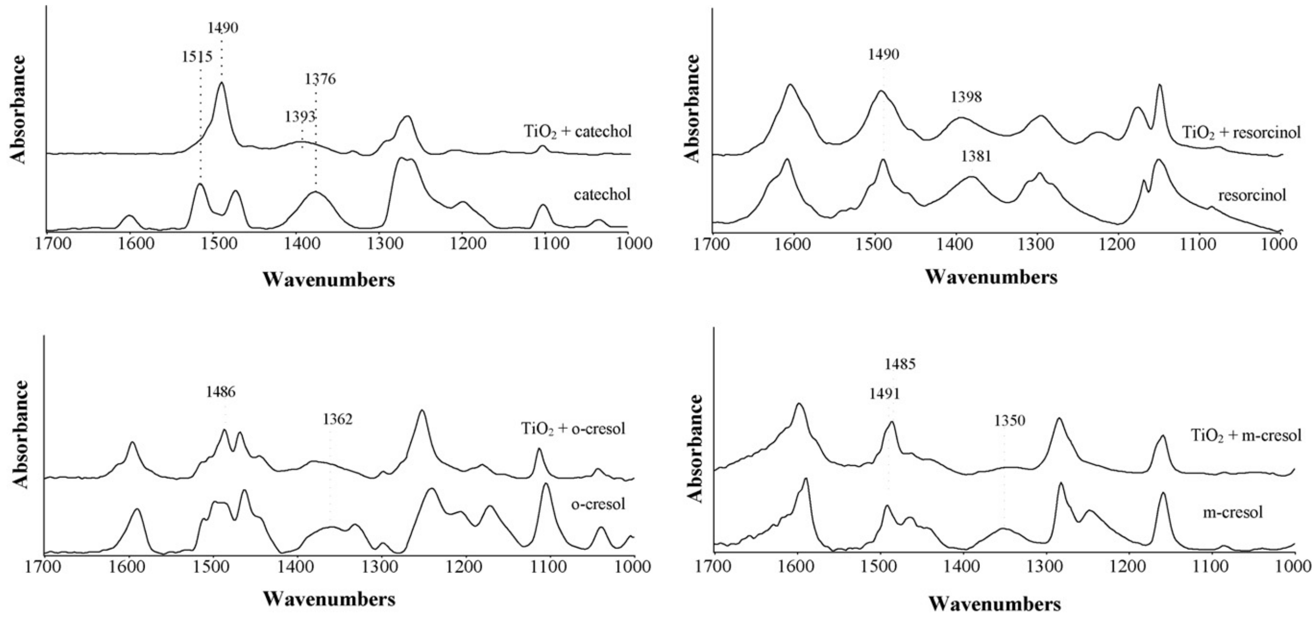
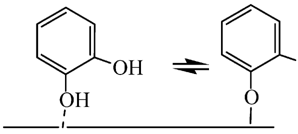


Fig. 8. (a) FTIR spectrum from catechol interactions with TiO_2 in the regions between 1700 and 1000 cm^{-1}. Catechol reference spectrum is also shown. (b) FTIR spectrum from resorcinol interactions with TiO_2 in the regions between 1700 and 1000 cm^{-1}. Resorcinol reference spectrum is also shown. (c) FTIR spectrum from *o*-cresol interactions with TiO_2 in the regions between 1700 and 1000 cm^{-1}. *o*-Cresol reference spectrum is also shown. (d) FTIR spectrum from *m*-cresol interactions with TiO_2 in the regions between 1700 and 1000 cm^{-1}. *m*-Cresol reference spectrum is also shown. (e) FTIR spectrum from phenol interactions with TiO_2 in the regions between 1700 and 1000 cm^{-1}. Phenol reference spectrum is also shown.

Results shown in Fig. 8a indicate that the interaction of catechol generates a monodentate catecholate (intensity reduction and δOH band shift from 1376 to 1393 cm^{-1}) [29,30] (structure I). Likewise, a notable change of the relative intensity of νC–O vibration (bands between 1300 y 1165 cm^{-1}) was observed.

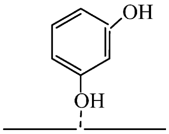
An important νC=C vibration band shift towards lower wavenumbers (from 1511 to 1490 cm^{-1}) must be stressed because it implies a notable electrodonation reduction with respect to the catechol reference spectrum [31].



structure I

In the spectrum from resorcinol-TiO_2 interaction (Fig. 8e), only small band shifts were observed, such as that from δOH (from 1381 to 1398 cm^{-1}) and νC=C (from 1490 to 1492 cm^{-1}) vibrations. In this case, νC–O (1295 cm^{-1}) vibration band remained unaltered.

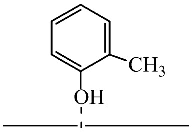
These results suggest that the interaction occurs through hydrogen bond as shown in structure II [30].



structure II

The interaction of *o*-cresol produces a significant intensity reduction of the band attributed to δOH vibration (1362 cm^{-1}) and changes in the vibration νC–O (1300–1165 cm^{-1}) (Fig. 8e).

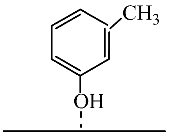
However, as in the previous case, changes of the band attributed to νC=C (1486 cm^{-1}) vibration were not observed, indicating that the electrodonation to the aromatic ring after interaction (structure III) was not altered.



structure III

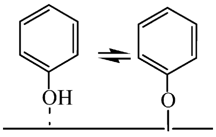
As observed with *m*-cresol, the relative intensity of the band attributed to δOH vibration (1350 cm^{-1}) (Fig. 8d) was notably reduced.

However, the νC=C vibration band was slightly shifted from 1491 to 1485 cm^{-1}, suggesting a small reduction in electrodonation to the aromatic ring (structure IV).



structure IV

In addition to this, the spectrum of phenol (Fig. 8e) showed a change in δOH (1392 and 1370 cm^{-1}) relative intensity and an important shift of the νC=C vibration band from 1495 to 1485 cm^{-1}. These results reveal that phenol–TiO_2 interaction results in a remarkable electrodonation reduction (structure V).



structure V

According to these FTIR results, the number and intensity of activating positions of the studied phenolic compounds is given by the following sequence:

resorcinol > *m*-cresol > *o*-cresol > catechol ≥ phenol

However, in the experiments with their mixtures $r_{\mathrm{C(R)}}$ was higher than $r_{\mathrm{R(C)}}$ in all the studied concentration range. The same occurred with $r_{\mathrm{C}(m\text{-}\mathrm{C})}$ and $r_{m\text{-}\mathrm{C(C)}}$ or $r_{\mathrm{C}(o\text{-}\mathrm{C})}$ and $r_{o\text{-}\mathrm{C(C)}}$. Consequently, if in these mixtures degradation rates are determined by the affinity for the photogenerated radicals as a function of the intensity and number of activating positions, thus the resulting catalytic behaviour would be the opposite to that observed. As a consequence, the observed photocatalytic behaviour must be interpreted from a different point of view.

In previous studies we have determined that catechol and resorcinol molecules tend to adsorb at different centers [30]. Thus, it was indicated that catechol interacts with isolated hydroxyl groups present at the surface of TiO_2, while resorcinol is likely to interact with interbonded hydroxyl groups. These results are supported by the adsorption experiment results of this work, in which almost no differences were observed in the mixtures in comparison with the individual compounds within the studied concentration range.

The isolated hydroxyl groups have been considered to be the most photoactive due among other factors to their basicity [26–28]. Thus, the interaction of catechol with these groups can be the main cause of the notable degradation rate diminution of the other phenolics exerted by this compound.

Nonetheless, as mentioned above the degradation rates of resorcinol, the cresols and phenol were reduced in the presence of other phenolic compounds than catechol, although to a lesser extent. In these cases, it has been pointed out that the observed degradation rate reduction was of the same order of magnitude than those obtained in the experiments without air or under nitrogen atmosphere. Hence, it is possible that the presence of other phenolic compound alters the photoadsorption of oxygen and consequently the resulting degradation rate.

Furthermore, the interaction of catechol with the $^{\bullet}$OH forming hydroxyls inhibits reaction (2) and consequently H_2O_2 deactivation. As a result, without air and at high concentrations of catechol its degradation rate was not modified (Fig. 6). Contrary to this, in the presence of H_2O_2, without air and at low concentrations, degradation rates were notably augmented. This can be understood by considering that under these conditions not enough molecules of catechol were available to neutralize the $^{\bullet}$OH forming hydroxyls, resulting in a non negligible effect of air by means of the reaction indicated in Scheme 1

4. Conclusions

The study of mixtures of phenolic compounds have shown that the specific adsorption centres for these compounds exert a more important effect on their degradation rate than the number of molecules adsorbed or the number of activating positions generated by their respective substituents.

It has been shown that the interaction of catechol with $^{\bullet}$OH forming hydroxyls ($\mathrm{OH}^{-}{}_{(\bullet}\mathrm{OH})$) results in the slowing down of the degradation rates of the other phenolic compounds.

Additionally, the results obtained suggest that the interaction of each compound with TiO_2 surface generates a specific surface distribution for oxygen photoadsorption. As a consequence, it seems that in mixtures of these compounds, oxygen photoadsorption is altered resulting in modified degradation rates.

The effect of oxygen photoadsorption was clearly correlated with degradation rate changes of the mixtures in comparison with their individual reactions in the presence of H_2O_2.

Finally, it has been shown that the interaction of catechol with ($\mathrm{OH}^{-}{}_{(\bullet}\mathrm{OH})$) inhibits H_2O_2 deactivation (reaction (2)) and the effect of air on the regeneration of these hydroxyl groups.

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