Photocatalytic degradation of phenol and phenolic compounds
Part I. Adsorption and FTIR study

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Abstract

With the goal of predicting the photocatalytic behaviour of different phenolic compounds (catechol, resorcinol, phenol, *m*-cresol and *o*-cresol), their adsorption and interaction types with the TiO$_2$ Degussa P-25 surface were studied.

Langmuir and Freundlich isotherms were applied in the adsorption studies. The obtained results indicated that catechol adsorption is much higher than those of the other phenolics and its interaction occurs preferentially through the formation of a catecholate monodentate. Resorcinol and the cresols interact by means of hydrogen bonds through the hydroxyl group, and their adsorption is much lower than that of catechol. Finally, phenol showed an intermediate behaviour, with a Langmuir adsorption constant, K_L, much lower than that of catechol, but a similar interaction.

The interaction of the selected molecules with the catalyst surface was evaluated by means of FTIR experiments, which allowed us to determine the probability of $^\bullet$OH radical attack to the aromatic ring.
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1. Introduction

The use of phenol and phenolic compounds in industrial processes and their presence in the resulting wastewaters is an issue of environmental concern. Their high toxicity, even at low concentrations, has motivated the search and improvement of many treatment techniques. In this sense, photocatalysis can yield feasible, convenient methods for the treatment of phenolic wastewaters. Thus, phenol photocatalytic degradation has been widely studied [1–10].

The application of catalytic techniques to waste treatment demands a deep knowledge of catalyst surface features, such as surface area, hydroxylation degree, crystallinity or pore size.

Additionally, in photocatalytic processes, the proximity between adsorption and photoactive centres also determines reaction rate [11]. As adsorption seems to be specific, different molecules can adsorb at different centres. Thus, it is useful to carry out adsorption-degradation experiments for each organic under examination. In fact, degradation depends on the molecule inter-action as determined by its functional groups. This suggests that the photocatalytic behaviour of contaminants with similar functional groups may not be easily predicted. It has been indicated that certain adsorbates can interact with active centres such as hydroxyl groups or bridging oxygen on TiO$_2$ surface, resulting in a different catalytic activity [12]. Also, some of them can act as poisons [13–17]. In addition to this, modified structural defect concentrations or reduced surface area will affect phenol, anisole and pyrimidine photocatalytic degradations at different extents [18].

In this paper, a thorough comparative study on the adsorption and interaction type of phenol and phenolic compounds (catechol, resorcinol, *m*-cresol and *o*-cresol) was carried out with

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the aim of determining how these variables could affect their photocatalytic degradation.

2. Experimental

2.1. Materials

Phenol was from Merck (1.00206.1000 ZA2592606 829, purity >99.5%). Catechol and resorcinol were from Aldrich (13501-1, 99+%) and (39804-7, 99+%), respectively. *m*-Cresol and *o*-cresol were from Fluka (00656, 99+%) and (606990, 99.5+%), respectively. pH was adjusted with diluted H_2SO_4 from Scharlau (AC20071, 96% ± 0.1). Acetonitrile and acetic acid were from Scharlau (AC0324, 99.85+%) and Panreac (131008, 99.7+%). TiO_2 was Degussa P-25 TiO_2 powder (80% anatase and 20% rutile).

2.2. Equipment

Remaining phenolics concentrations at different adsorption times were HPLC-measured using a Macherey-Nagel CC 250/4 NUCLEOSIL 100-5 PROTECT 1 and an acetonitrile–water–acetic acid (40:59.5:0.5) mobile phase, using a UV detector ($\lambda = 270$ nm).

A FTIR spectrophotometer model RS/1 (UNICAM) was used for spectral analysis. Spectra were obtained in the 1550–1300 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.

2.3. Adsorption studies

The adsorption studies were performed in the darkness with aqueous suspensions containing 10–150 ppm of phenol, catechol, resorcinol, *m*-cresol or *o*-cresol and 2 g/L catalysts (Degussa P-25 TiO_2) in continuously stirred 250 mL glass vessels. All the experiments were performed at pH 5 and constant temperature of 25 °C. Samples (3 mL) were taken for the analyses. The equilibrium concentration was determined by HPLC after filtration with Millipore (0.45 μm pore diameter) syringe
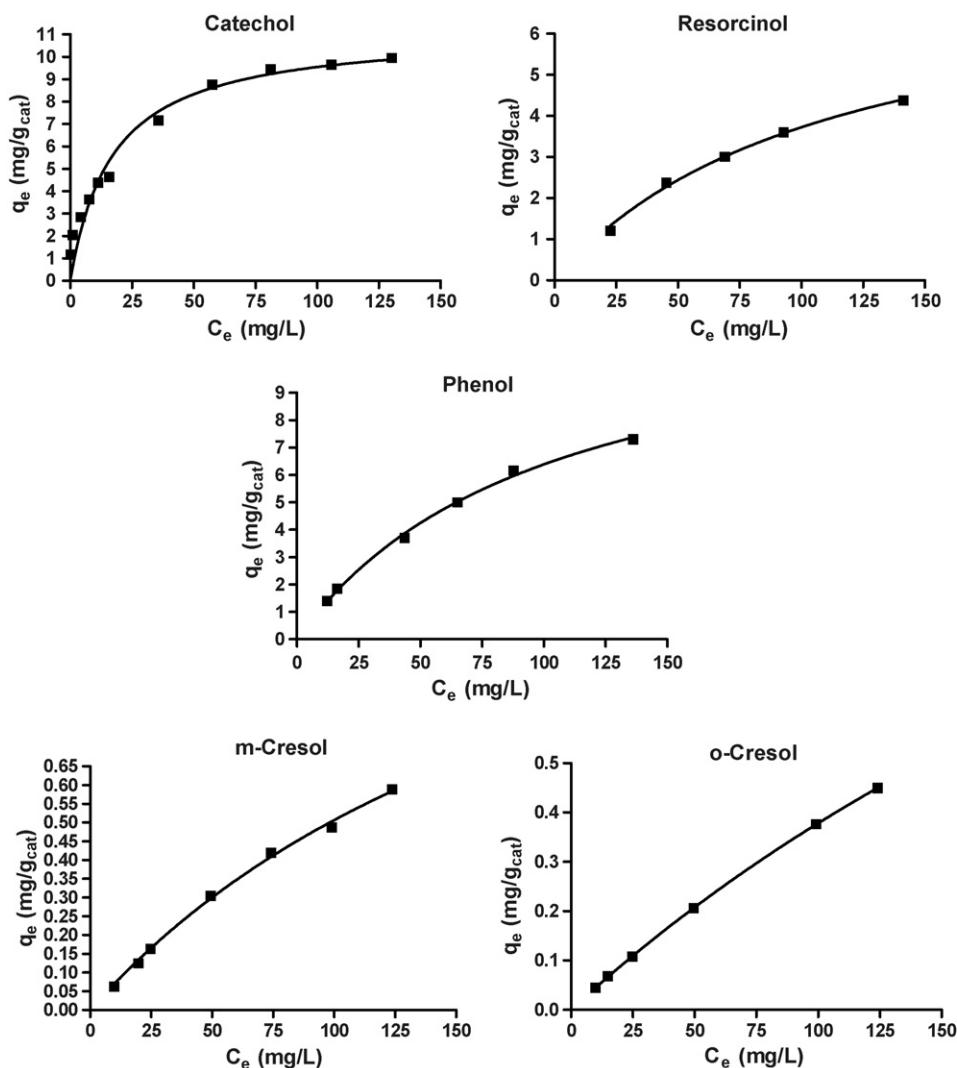

Fig. 1. Catechol, resorcinol, phenol, *m*-cresol and *o*-cresol isotherms obtained as non-lineal representation of Langmuir model.

filters. These experiments lasted also 2 h and samples were taken every 15 min. As in other studies [19] no adsorption changes were observed after the first 30–45 min.

Langmuir and Freundlich isotherms were used to quantify the adsorption of the organics on TiO$_2$ surface.

K_L and Q_L were determined by means of a non-lineal regression fit of the Langmuir equation:

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e}$$

where q_e is the amount of solute adsorbed by gram of TiO$_2$, K_L the Langmuir equilibrium constant, Q_L the adsorption maximum capacity of the solute on the TiO$_2$ surface and C_e is the solute concentration in the equilibrium.

The values of n_F were determined from the lineal regression of the logarithmics of the Freundlich equation:

$$q_e = K_F C_e^{n_F}$$

where K_F is the Freundlich constant relative to the adsorbent specific surface and n_F is the Freundlich constant relative to the average adsorption energy [20].

3. Results and discussion

3.1. Adsorption studies

As mentioned in Section 1, adsorption is a fundamental process in photocatalysis. Different authors have correlated the photocatalytic activity with adsorption changes of the studied compound [21–23]. Our goal in this study was to determine the effect of adsorption and interaction intensity on the photocatalytic degradation of phenol and some phenolic compounds. Langmuir and Freundlich models were used to determine the adsorption capacity and interaction intensity of each compound, respectively.

Figs. 1 and 2 show the obtained catechol, resorcinol, phenol, *m*-cresol and *o*-cresol isotherms as non-lineal and lineal representations of Langmuir and Freundlich models, respectively. Table 1 shows the obtained values of C_e, Q, n and R^2. For the concentration domain studied, catechol adsorption isotherm (Fig. 1) can be considered a type I. This suggests that catechol can interact with all the accessible sites of TiO$_2$ surface. However, the obtained isotherms for the other
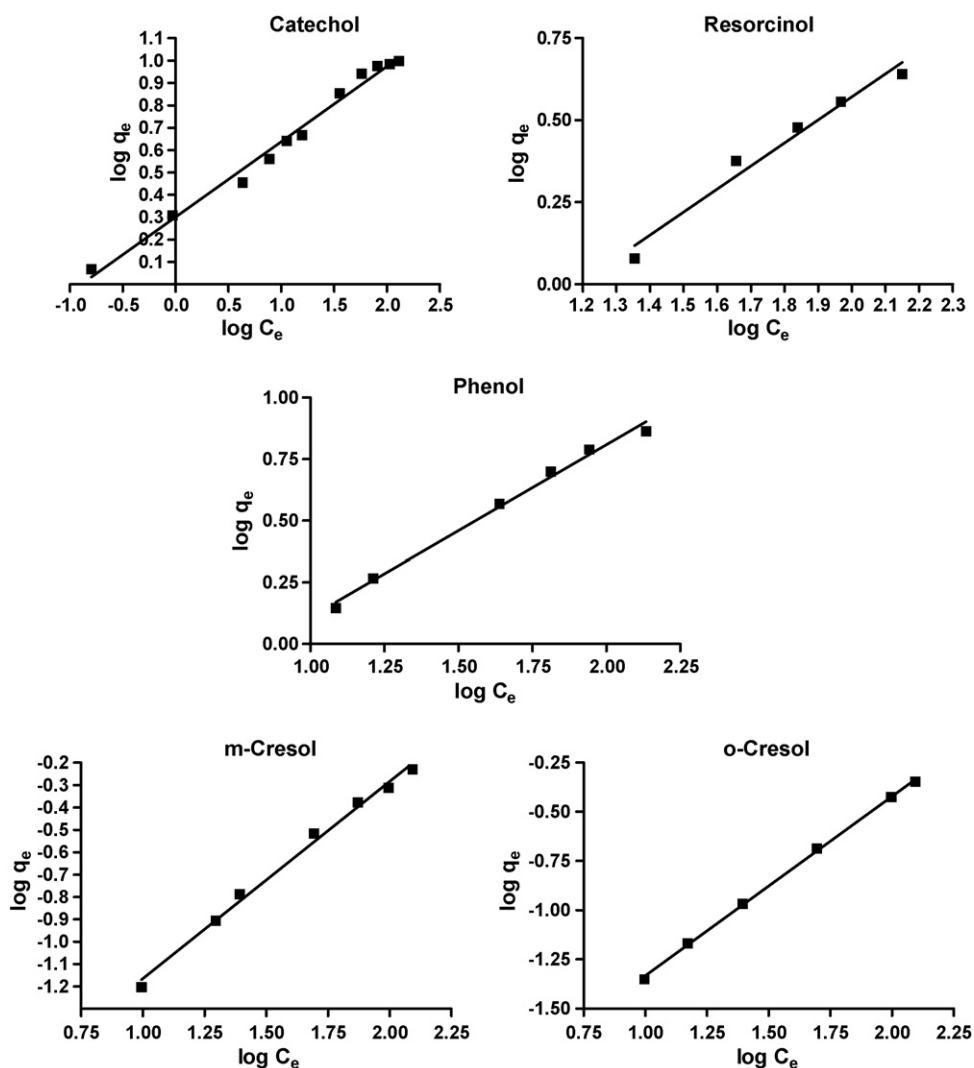

Fig. 2. Catechol, resorcinol, phenol, *m*-cresol and *o*-cresol isotherms obtained as lineal representation of Freundlich model.

phenolics are similar to those from other studies [20] where their description is considered to be more complex. In these cases, it is assumed that the Langmuir equation is valid up to a concentration limit, which is characteristic of each phenolic compound.

The catechol adsorption constant obtained from Langmuir model was much larger than those of the other compounds, while that of phenol was slightly larger than that of resorcinol. This is in agreement with other studies [24–26]. In fact, it has been indicated that catechol can adsorb at different centres [27]. Thus, the following sequence was obtained:

$$K_L^{catechol} \gg K_L^{phenol} > K_L^{resorcinol} > K_L^{m-cresol} > K_L^{o-cresol}$$

As observed by other authors with different phenolic compounds, the isotherms also obey the Freundlich equation. This has been interpreted as the strength of the energy of adsorption varying with the covering degree. As indicated above, in this equation the value of n_F is correlated with the aver-

Table 1
Langmuir and Freundlich parameters for phenolic compounds studied

	K_L (mg/L)	Q_L (mg/g$_{cat}$)	R_L^2	n_F	R_F^2
Catechol	0.0585	11.172	0.972	0.337	0.987
Resorcinol	0.0089	7.870	0.995	0.703	0.972
Phenol	0.0098	12.882	0.997	0.699	0.992
m-Cresol	0.0045	1.623	0.997	0.881	0.993
o-Cresol	0.0021	2.105	0.999	0.911	0.999

age adsorption energy, being higher the solid-adsorbate affinity at lower n_F values. Thus, form the n_F values obtained from the Freundlich isotherms (Table 1), the following sequence results:

$$n_F^{catechol} \gg n_F^{phenol} > n_F^{resorcinol} > n_F^{m-cresol} > n_F^{o-cresol}$$

This sequence is the same as the obtained from K_L. However, the maximum quantity adsorbed (Q_L) does not follow the same sequence. This is due to the fact that the higher the Langmuir
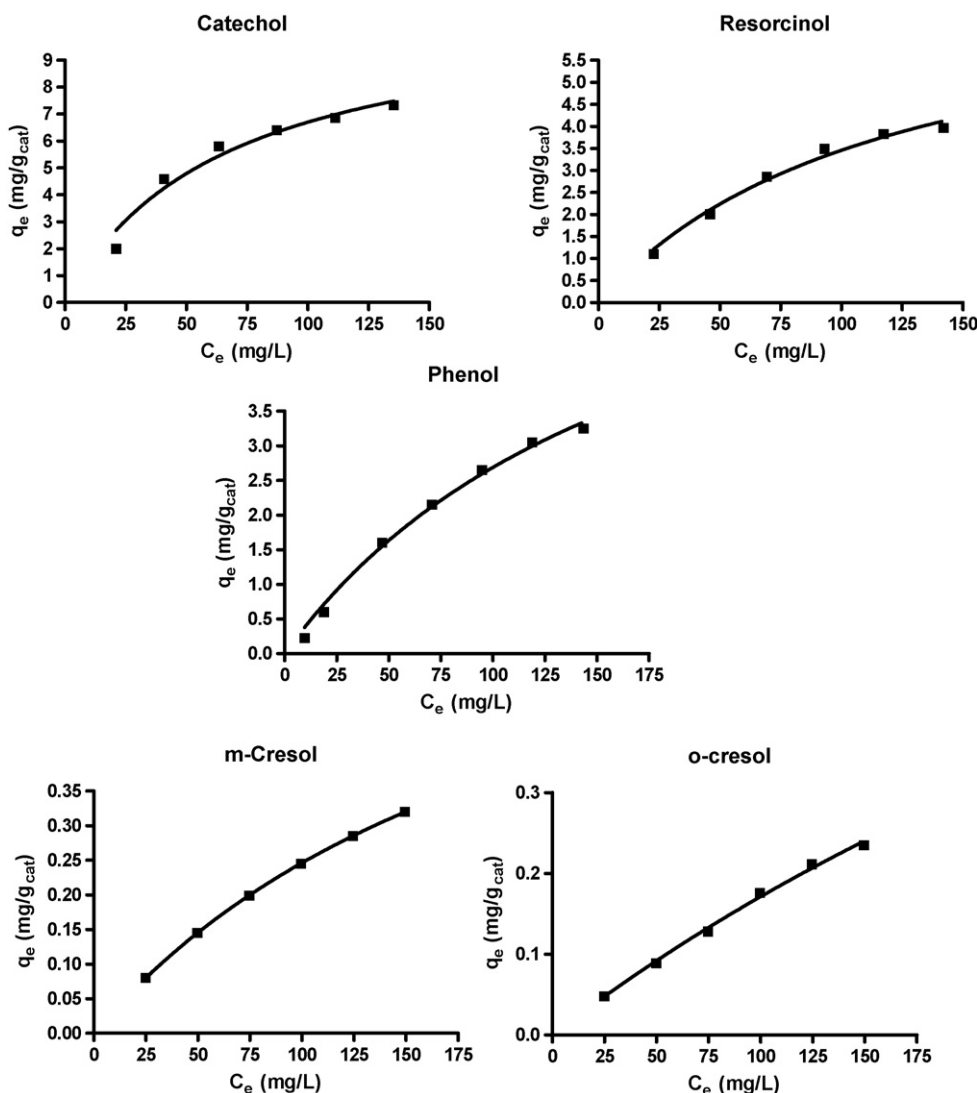

Fig. 3. Catechol, resorcinol, phenol, m-cresol and o-cresol isotherms, in the presence of H$_2$O$_2$, obtained as non-lineal representation of Langmuir model.
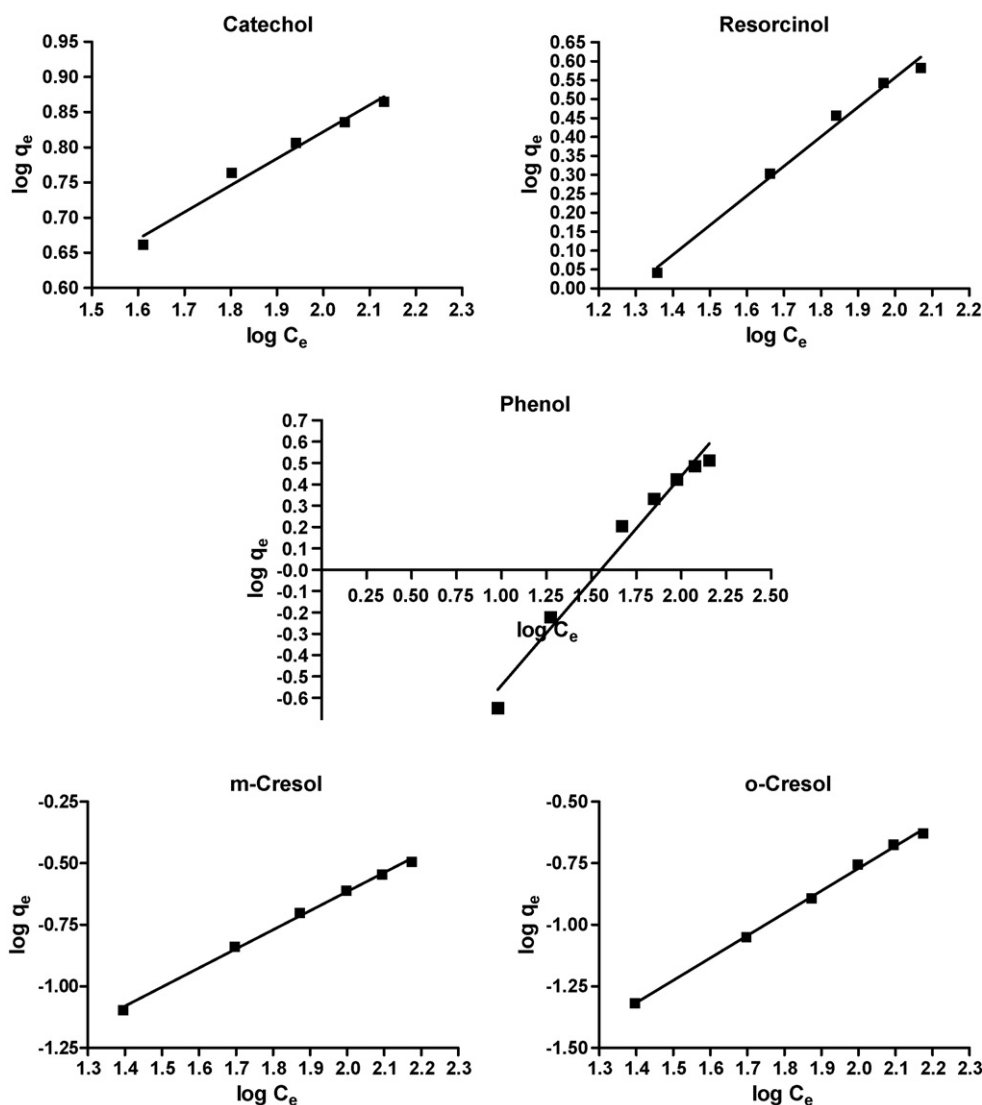
Fig. 4. Catechol, resorcinol, phenol, *m*-cresol and *o*-cresol isotherms, in the presence of H_2O_2, obtained as lineal representation of Freundlich model.

adsorption constant (or the Freundlich energetic index, n_F) the lower amount of the substrate will be necessary to saturate the solid's surface, Q_L.

H_2O_2 can enhance photocatalytic activity by scavenging photogenerated electrons to yield $^\bullet OH$ radicals [28,29]. Nonetheless, in different studies the presence of H_2O_2 does not provide the expected effect. This has been attributed to different processes [30,31]. With the goal of determining possible competition for the adsorption centres between H_2O_2 and the phenolics, the same adsorption experiments were carried out in the presence of H_2O_2 (2 g/L). The obtained Langmuir and Freundlich isotherms are shown in Figs. 3 and 4, respectively. Table 2 shows the corresponding values of K_L, Q_L and n_F.

The adsorption constants (K_L) for catechol and phenol resulted to be considerably reduced with respect to those obtained in the absence of the oxidiser (Table 1). Those for resorcinol and the cresols remained almost unmodified. The adsorption constant for catechol is still the largest. Nevertheless,

the values of n_F were roughly the same, being notably increased only for phenol.

3.2. FTIR studies

The results from the Freundlich indicate that n_F, which is related with the average adsorption energy, is highly dependent on the studied compound. With the goal of gaining a better under-

Table 2
Langmuir and Freundlich parameters for phenolic compounds studied in the presence of H_2O_2

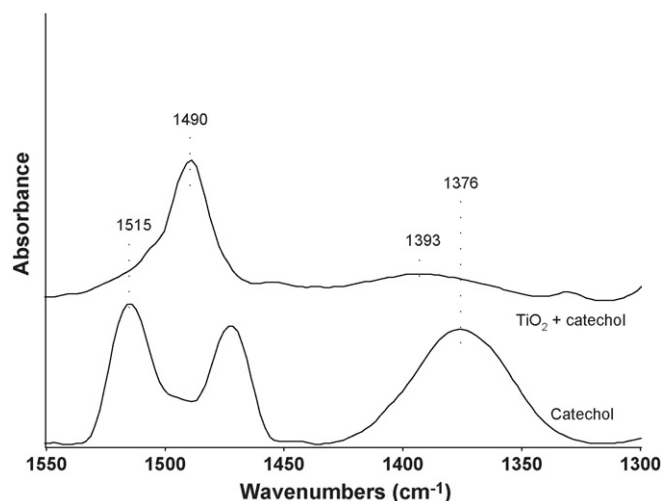|	K_L (mg/L)	Q_L (mg/g_{cat})	R_L^2	n_F	R_F^2
Catechol	0.0150	11.140	0.964	0.38	0.977
Resorcinol	0.0083	7.605	0.986	0.781	0.991
Phenol	0.0054	7.583	0.993	0.979	0.979
m-Cresol	0.0044	0.804	0.999	0.774	0.997
o-Cresol	0.0015	1.242	0.996	0.908	0.998

Fig. 5. FTIR spectrum from catechol interactions with TiO$_2$ in the regions between 1550 and 1300 cm^{-1}. Catechol reference spectrum is also shown.

Fig. 7. FTIR spectrum from o-cresol interactions with TiO$_2$ in the regions between 1550 and 1300 cm^{-1}. o-Cresol reference spectrum is also shown.

standing of the interaction sort of each compound with the TiO$_2$ surface, FTIR studies were carried out.

Figs. 5–9 show FTIR spectra from catechol, resorcinol, o-cresol, m-cresol and phenol interactions with TiO$_2$ between 1550 and 1300 cm^{-1}. This IR region was selected to emphasize the variation of δOH and νC=C vibrations after the interaction. δOH vibration band modifications or disappearance would reveal the compound interaction sort, i.e., by means of a hydrogen bond or the formation of a phenolate. Additionally, shifts of the first νC=C vibration band component (1510–1470 cm^{-1}) towards lower wavenumbers, would indicate an electrodonation reduction to the ring as consequence of the molecule interaction with TiO$_2$ surface. However, a band shift towards higher wavenumbers would indicate an electrodonation increment [32].

Results shown in Fig. 5 indicate that catechol interaction generates a catecholate monodentate (intensity reduction and δOH
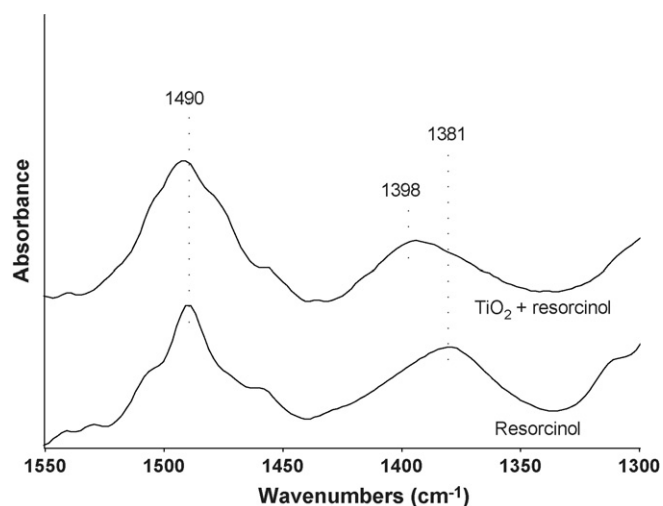

Fig. 8. FTIR spectrum from m-cresol interactions with TiO$_2$ in the regions between 1550 and 1300 cm^{-1}. m-Cresol reference spectrum is also shown.

Fig. 6. FTIR spectrum from resorcinol interactions with TiO$_2$ in the regions between 1550 and 1300 cm^{-1}. Resorcinol reference spectrum is also shown.

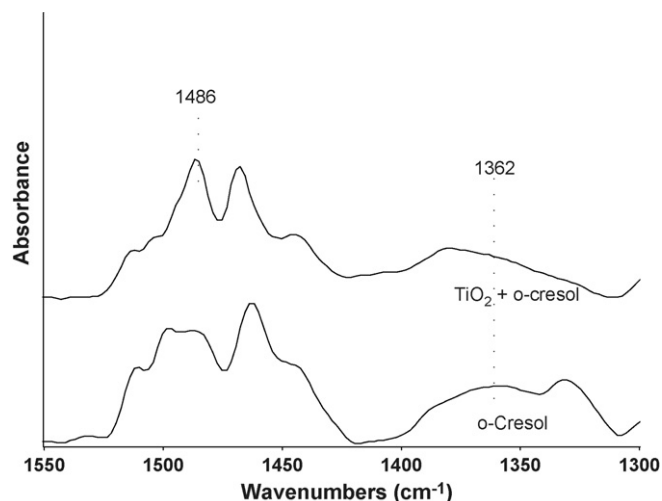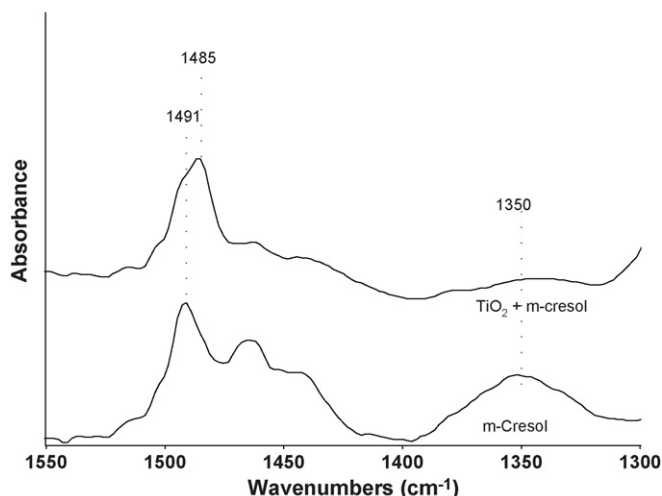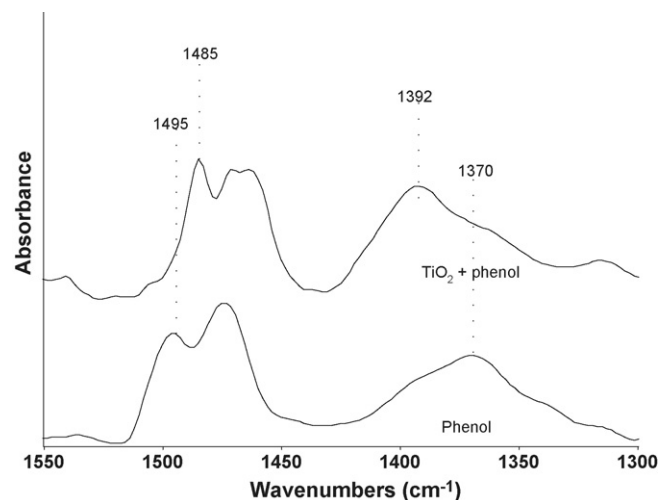Fig. 9. FTIR spectrum from phenol interactions with TiO$_2$ in the regions between 1550 and 1300 cm^{-1}. Phenol reference spectrum is also shown.

band shift from 1376 to 1393 cm^{-1}) [24,27] (structure I). An important νC=C vibration band shift towards lower wavenumbers (from 1515 to 1490 cm^{-1}) must be stressed because it implies a notable electrodonation reduction with respect to the catechol reference spectrum.

structure I
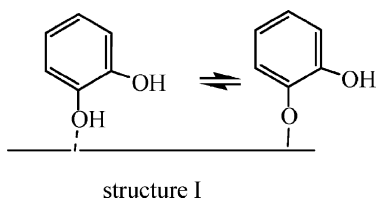
In the resorcinol–TiO$_2$ interaction spectrum (Fig. 6), only small band shifts are observed, such as that from δOH (from 1381 to 1398 cm^{-1}) and νC=C (from 1490 to 1492 cm^{-1}) vibrations. These results suggest that interaction occurs through hydrogen bond (structure II) [27].


structure II
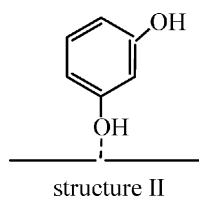
o-Cresol interaction produces an important intensity reduction of the band attributed to δOH vibration (1362 cm^{-1}) (Fig. 7). However, as in the previous case, changes of the band attributed to νC=C (1486 cm^{-1}) vibration are not observed, indicating that electrodonation to the aromatic ring after interaction (structure III) is not altered.

structure III
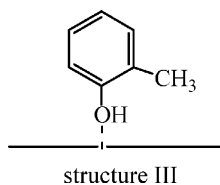
Also in the case of *m*-cresol, the relative intensity of the band attributed to δOH vibration (1390 cm^{-1}) (Fig. 8) is notably reduced. However, the νC=C vibration band is slightly shifted, from 1491 to 1485 cm^{-1}, indicating a small reduction in electrodonation to the aromatic ring (structure IV).

structure IV
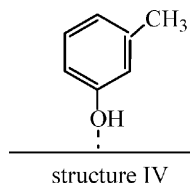
In addition to this, phenol spectrum (Fig. 9) shows a change in δOH (1392 and 1370 cm^{-1}) vibration band relative intensity and an important shift of the νC=C vibration band, from 1495 to 1485 cm^{-1}. These results indicate that phenol–TiO$_2$ interaction results in a remarkable electrodonation reduction (structure V).

structure V
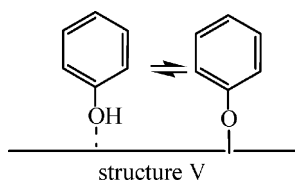
4. Discussion

According to several authors [33,34], Ti^{4+} atoms present on the TiO$_2$ hydrated surface must be completely coordinated by hydroxyl groups and water molecules in an approximate proportion of 50%. Under these conditions, there are no voids for oxygen fixation. Thus, $^{\bullet}$OH radical formation on TiO$_2$ surface can be illustrated as in Scheme 1.

The first process step would consist of the hydroxyl reaction with photogenerated holes. It has been indicated that strongly basic, isolated hydroxyls are the most photoactive, though photoactivity of other less basic hydroxyls or even adsorbed water molecules, is not discarded.

This reaction acts as a trigger of a set or reactions that start with adsorbed water molecule desorption to leave spare centres for O$_2$$^-$ photo-adsorption. If adsorbed organics such as phenolics are close to photoactive centres, they can be attacked by these radicals but depending on the organic-radical affinity. Phenolics degradation rate is determined by the ability of the substituents at generating ring activating or deactivating positions for $^{\bullet}$OH radical attack [25,35,36]. This is determined by the Hammet constant, with more negative values indicating larger ring activation and consequent attack probability. The Hammet constant for –OH groups is −0.37, while that for methyl group is −0.17. Moreover, some studies have confirmed that in addition to $^{\bullet}$OH radicals, these compounds can react directly with photogenerated holes and O$_2$$^{\bullet-}$ radicals, being the later ones a less relevant process [37,38].

Consequently, resorcinol and *m*-cresol substituents can generate three doubly activating positions. Since Hammet constant is larger for hydroxyl than for methyl group, resorcinol activation will be more intensive than that of *m*-cresol. Moreover, catechol and *o*-cresol substituents generate four activating positions, being more intensive in the former. Phenol can generate three activating positions. Nevertheless, as a general rule, interaction with TiO$_2$ surface can vary activation intensity. Thus, FTIR studies indicate that catechol can interact by means of a catecholate monodentate, thus notably reducing electrodonation. In fact, the larger value of n_F, which indicates the average adsorption energy, was obtained from catechol–TiO$_2$ surface interaction. Nonetheless, *o*-cresol interacts by H-bonds resulting in a much lower electrodonation diminution. Resorcinol and *m*-cresol also seem to interact by H-bonds with almost no electrodonation modification. Phenol interaction is a mixture between phenolate formation and H-bond, resulting as in the case of catechol in an important electrodonation decrease.

Considering the above, it could be concluded that the ability to generate aromatic ring activating positions in contact with TiO$_2$ surface would follow the sequence: resorcinol > *m*-cresol > *o*-cresol > catechol ≥ phenol.

However, in addition to the interaction type and intensity, the photocatalytic activity is determined by the molecule accessibility to the catalyst surface. This was determined by adsorption studies. In this case, the obtained sequence was significantly different from that resulting from the aromatic ring activating positions.
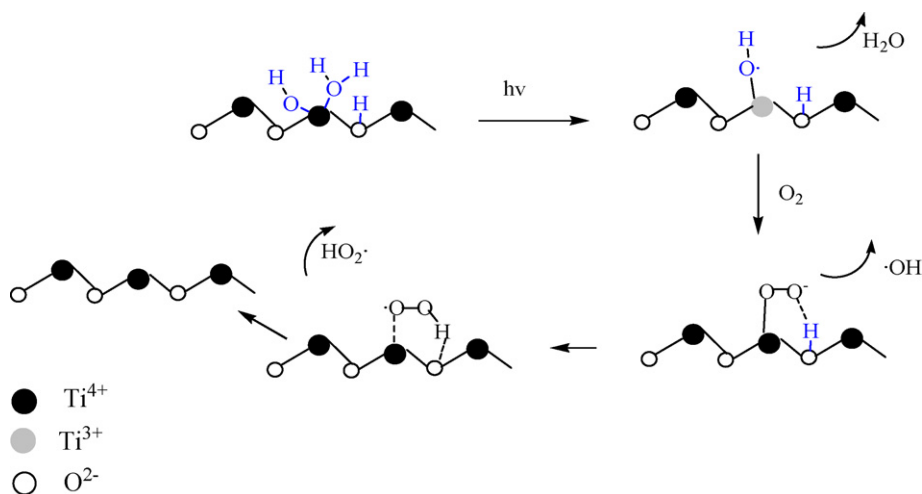
Scheme 1.

5. Conclusions

The obtained Langmuir and Freundlich isotherms have revealed that in the concentration domain studied:

- The adsorption of catechol, with higher adsorption constant (K_L) and average adsorption energy, was different from those of the other compounds studied.
- The cresols showed the lowest adsorption capacity.
- The presence of an oxidiser such as H_2O_2, notably altered K_L of catechol and phenol, while those of the other compounds remained almost unmodified.

According to the FTIR studies, the probability of aromatic ring attack by $^\bullet OH$ radicals followed the sequence: resorcinol > m-cresol > o-cresol > catechol $\geq$ phenol.

Finally, it must be stressed that adsorption and ability at generating aromatic ring activating positions yield completely different sequences. This should be taken into account for future studies on photocatalytic activity.

Acknowledgement

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