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Role of Cu in the Cu-TiO_2 photocatalytic degradation of dihydroxybenzenes

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Abstract

The photocatalytic degradation of three dihydroxybenzenes (hydroquinone, catechol and resorcinol) by TiO_2 and Cu-TiO_2 has been studied. Degradation rates depend on the molecule catalyst surface interaction type. FTIR studies have shown that Cu presence modifies the organics interactions with the catalysts surface. Therefore, catalysts have shown different types of behaviour with each compound.

Resorcinol interaction with Cu-TiO_2 may produce a hydroxyphenolate thus reducing the number of activating centres in the aromatic ring. However, catechol interaction provides a catecholate bidentate which virtually deactivates the aromatic ring, hence reducing its degradation by $^{\bullet}OH$ radicals attacks. Hydroquinone interaction with Cu-TiO_2 occurs by means of a hydrogen bond, while with TiO_2 this interaction is established through the formation of a hydroxyphenolate monodentate. This justifies the improved catalytic behaviour of Cu-TiO_2.

Studies in presence of H_2O_2 have shown the existence of similar degradation mechanisms, but degradation rates have been notably higher.

Keywords: Photocatalysis; Cu-TiO_2; Dihydroxybenzenes; TiO_2

1. Introduction

The adsorption of a fluid (gas or liquid) molecule on a solid catalyst surface may determine the effectiveness of the overall process. In fact, it has been observed that either new atoms or molecules located on the catalyst surface may promote opposite effects on nearby molecules or atoms [1–4]. In heterogeneous catalysis, a compound degradation rate depends on its ability to adsorb on the catalyst surface [5,6]. For example, dye molecules adsorption is required for their degradation [7]. Additionally, the competition for adsorption centres between water molecules and those to be degraded plays an important role in photocatalysis [8].

However, many authors have not found a direct relationship between adsorption and photodegradation. In some cases, the adsorption of compounds or intermediates on the catalyst surface may act as poisons [9]. Also, it has been suggested that the photo-generated oxidising species do not migrate far away from active centres where they are formed. Therefore, degradation occurs on the surface or at few nanolayers around photocatalytic particles [10].

Furthermore, electron–hole recombination also plays a crucial role. In fact, the use of TiO_2 as a photocatalyst in most of these processes accounts for their low recombination rate [11,12]. Nevertheless, such a recombination rate is still considered too fast, and several studies have been performed in an effort to reduce it through catalyst doping [13–17]. As indicated above, the presence of heterogeneous atoms on the TiO_2 surface may alter the catalyst features and consequently, its behaviour.

Numerous photocatalytic studies have been performed using Cu as TiO_2 dopant [18–24]. Thus, it has been indicated that Cu(II) may extend the light absorption to visible region [18], modify the TiO_2 valence band spectrum [20] and improve photocatalytic activity [19,21–23]. In this paper the effect of doping TiO_2 with Cu on the photodegradation of dihydroxybenzenes (hydroquinone, catechol and resorcinol) has been investigated. Moreover, in addition to monitoring the degradation of these compounds with and without H_2O_2,

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the organic interaction with catalyst surfaces has been studied by FTIR. Finally, the relation between organic–catalyst surface interactions and degradation mechanisms has been established.

2. Experimental

2.1. Catalyst preparation

TiO_2 was Degussa P-25 (80% anatase). Cu-TiO_2 was prepared by TiO_2 impregnation with $CuSO_4$ aqueous solutions (incipient wetness impregnation method) [25] at 298 K. First TiO_2 was mixed with an aqueous solution of $CuSO_4$. The TiO_2 + metal mixture was stirred for 48 h. Later, water was evaporated by heating it at 373 K over 24 h. Finally, the catalysts were calcined at 773 K for 5 h. Metallic precursor concentration was required to obtain 0.5% (w/w) of dopant. Also, a non-doped catalyst (bare-TiO_2) was prepared by the same calcination process for comparison purposes.

2.2. Experimental conditions

The following experimental conditions have been employed for all experiments: 250 mL cylindrical glass vessels reactors, 100 ppm dihydroxybenzene aqueous solutions and 1 g/L of catalysts. H_2O_2 concentration was 35% (w/w). Suspensions were continuously stirred. Also, before switching on the UV-lamp the suspension was stirred for 15 min to favour the organic chemisorption on the catalyst surface. For FTIR analysis catalysts were impregnated with 400 ppm hydroquinone, catechol or resorcinol aqueous solutions and placed after 15 min, between two CaF_2 windows for spectra acquisition.

2.3. Equipments

Remaining hydroquinone, catechol or resorcinol and reaction intermediates concentrations in different reaction times were HPLC-measured. A reverse phase column (C18 Macherey-Naggel E250-4), acetonitrile–water–acetic acid (29:70:1) mobile phase and a UV detector ($\lambda = 270$ nm) were employed.

A FTIR spectrophotometer model RS/1 (UNICAM) was used. Intervals from 2000 to 1000 cm^{-1}, a resolution of 2 cm^{-1} and forward and reverse moving mirror speed of 10 and 6.2 kHz, respectively, were used. Water reference spectrum was subtracted from every spectrum.

A 60 W UV-lamp (Philips Cleo HB 071) was employed as UV light source. The incident photon flux was measured by the ferrioxalate actinometry method [26] with a resulting photon flow of 1.26×10^{-6} einteins L^{-1} s^{-1}.

Dissolved copper was measured by a Zeeman Atomic Absorption Spectrophotometer from Varian, equipped with an automatic disperser and a graphite furnace.

3. Results

3.1. Degradation studies

Fig. 1 shows results obtained from hydroquinone, resorcinol and catechol degradations with bare-TiO_2 (Fig. 1(1)) and Cu-TiO_2 (Fig. 1(2)).

As may be observed, resorcinol achieves the highest degradation with bare-TiO_2 after 100 min. During the first 20 min. hydroquinone degradation rate resembles that of resorcinol, but later it is slowed down to that of catechol. Similar behaviour has been observed by other authors [27]. Accordingly, the obtained bare-TiO_2 degradation sequence is

$$\text{Resorcinol} > \text{hydroquinone} \approx \text{catechol} \qquad \text{(a)}$$

Nonetheless, Cu-TiO_2 achieves the highest degradation with hydroquinone after 100 min. Resorcinol degradation is intermediate between those of hydroquinone and catechol. In this case the Cu-TiO_2 degradation sequence is

$$\text{Hydroquinone} > \text{resorcinol} > \text{catechol} \qquad \text{(b)}$$

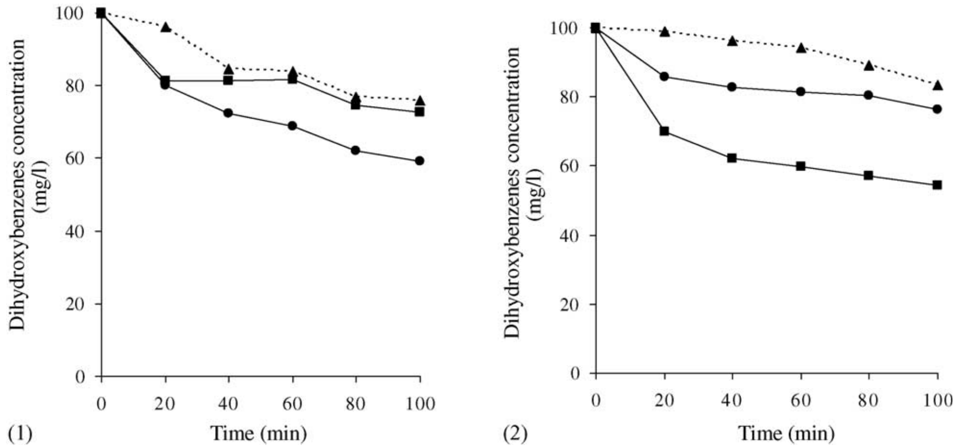


Fig. 1. Results from resorcinol (●), catechol (▲) and hydroquinone (■) degradations with bare-TiO_2 (1) and Cu-TiO_2 (2).

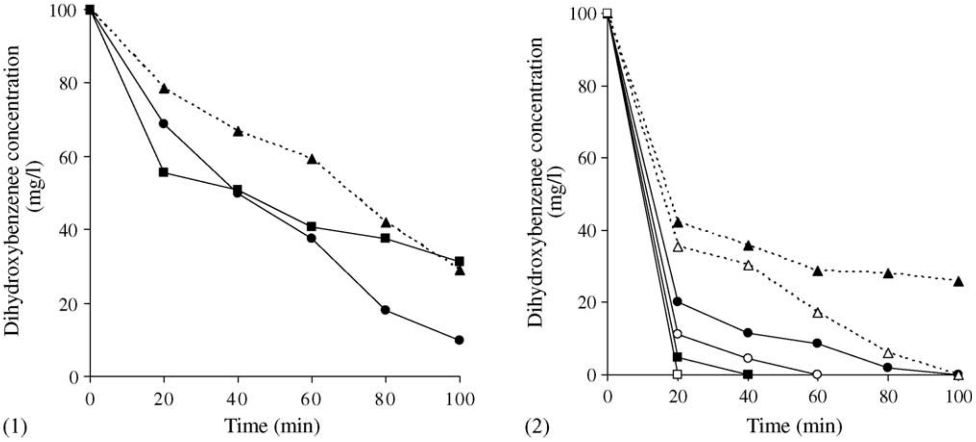


Fig. 2. Results from resorcinol (●, ○), catechol (▲, △) and hydroquinone (■, □) degradations with bare-$TiO_2 + H_2O_2$ ((1) full symbol), Cu-$TiO_2 + H_2O_2$ ((2) full symbol) and $Cu^{2+} + H_2O_2$ ((2) empty symbols).

It must be stressed that in all cases, degradation rates are most different during the initial minutes. After this time the process becomes slower. This could be due to the presence of new intermediates adsorbing on the catalyst surface.

The same experiments in the presence of 1.5 g/L H_2O_2 have been performed (Fig. 2). So, H_2O_2 may accept photogenerated electrons thus increasing degradation rate by [28,29]:

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

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \quad (2)$$

H_2O_2 addition notably improves the organics photodegradation, but under the same degradation sequences ((a) and (b)). Resorcinol and catechol degradations with bare-TiO_2 evolve at almost constant rates, but that of hydroquinone is fast during the first 20 min. and becomes subsequently slower. The same behaviour is observed without H_2O_2.

Furthermore, strong photodegradation during the first 20 min is achieved by combining H_2O_2 and Cu-TiO_2. Similar results have been obtained in the dark. In this case, this high initial reaction rate is attributed to the following reactions [30]:

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + O_2{}^{\bullet -} + 2H^+ \quad (3)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + HO^\bullet \quad (4)$$

However, after this initial period, degradation rates are slowed, mainly for catechol which becomes nil during the last 60 min.

The same experiments with 5 ppm Cu^{2+} aqueous solutions (the same Cu^{2+} concentration as that in Cu-TiO_2) + H_2O_2 have been carried out. Since a quite similar behaviour (Fig. 2(1)) has been observed, it may conclude that reactions (3) and (4) are responsible for such initial high reaction rates. Interestingly, also in these experiments, hydroquinone and resorcinol degradations are faster, particularly the former, with the catechol one significantly slower.

3.2. Atomic absorption studies

In previous studies with other doped catalysts, the dopant extraction during the photocatalytic reaction has been observed [31–33]. Consequently, to determine possible Cu extraction from Cu-TiO_2, the dissolved metal was analysed at different reaction times. In experiments without H_2O_2 only traces of the metal were obtained, but in those with H_2O_2 dissolved Cu concentrations were significant, particularly during the first 20 min with hydroquinone and resorcinol (Fig. 3).

However, obtained Cu concentration in experiments with catechol is significantly lower than those with hydroquinone and resorcinol. Experiments with Cu-$TiO_2 + H_2O_2$ but without the organics have revealed no metal extraction. Therefore, it seems that Cu–organic interaction, particularly resorcinol and hydroquinone, is necessary for the extraction to occur in presence of H_2O_2. This may be related to reactions (3) and (4) efficiencies.

These results show marked differences between bare-TiO_2 and Cu-TiO_2 in degrading the studied compounds. With bare-TiO_2, with and without H_2O_2, resorcinol

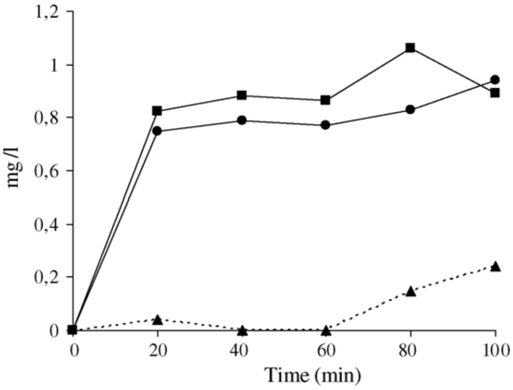


Fig. 3. Dissolved Cu concentration during resorcinol (●), catechol (▲) and hydroquinone (■) degradations with Cu-TiO_2.

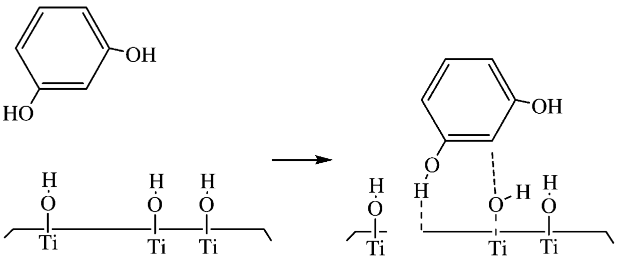
degradation is faster than that of hydroquinone, being the opposite with Cu-TiO_2. Nonetheless, catechol degradation is the slowest, especially with Cu-TiO_2. Experiments with H_2O_2 proved that the organics interaction with Cu^{2+} ions is required for the proposed reactions (3) and (4) to occur. To better explain these results, FTIR studies have been carried out on catalyst surface interaction with the selected compounds.

3.3. FTIR studies

3.3.1. Resorcinol

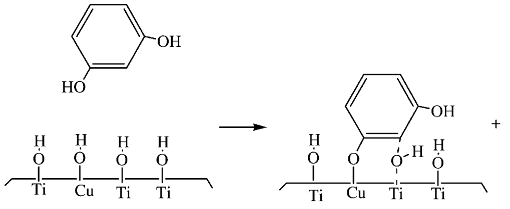
Fig. 4 shows the spectra from resorcinol interaction with the catalysts surface. The band attributed to δOH vibration (1381 cm^{-1}) is shifted towards higher wave numbers (1398 cm^{-1}). A new band, characteristic from aromatic *ortho*-substitutions [34,35], appears at 1225 cm^{-1} in the νC–OH vibration region.

Accordingly, resorcinol interaction with bare-TiO_2 by means of a hydrogen bond may be illustrated as follows:



(I)

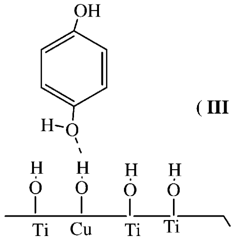
Additionally, in spectra from Cu-TiO_2 interaction with resorcinol, a considerable δOH vibration band intensity decrease and νC–O vibration band (1295 cm^{-1}) increase have been noticed. Also in this case, the band at 1225 cm^{-1} in the νC–OH vibration region is visible. Intensity changes observed in δOH and νC–O vibrations bands could indicate the following interactions:



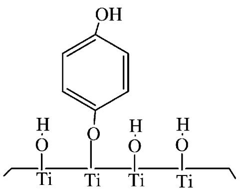
(II)

3.3.2. Hydroquinone

Spectra from hydroquinone interaction with the catalysts (Fig. 5) look quite similar. In both cases the band at 1606 cm^{-1} disappears and those at 1513 and 1474 cm^{-1} are shifted. These bands are attributed to νC–C vibrations in aromatic rings. Particularly in bare-TiO_2, δOH and νC–O vibration bands (1383–1366 and 1241–1223 cm^{-1}, respectively) intensities change. This may be indicative of the formation of a hydroxyphenolate monodentate on this catalyst, while in Cu-TiO_2 such a process is not so evident and a hydrogen bonding interaction may be proposed. Hence, the following interaction may be suggested:



(III)



(IV)

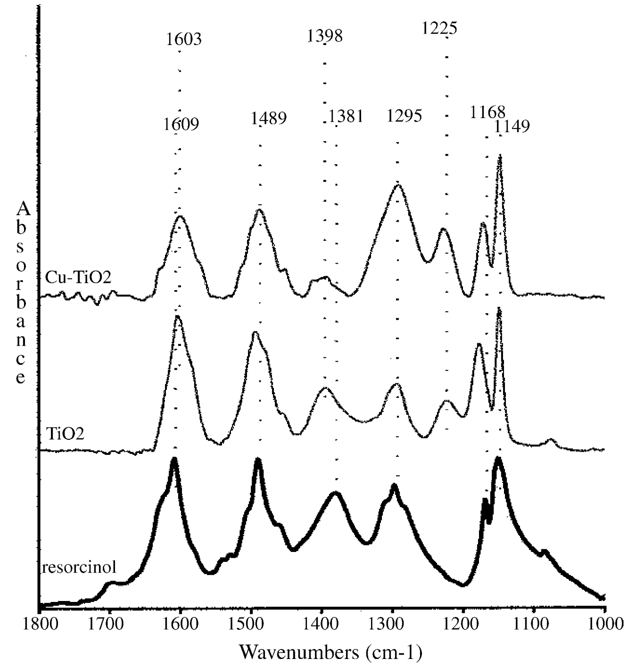


Fig. 4. IR spectra from resorcinol interaction with TiO_2 and Cu-TiO_2.

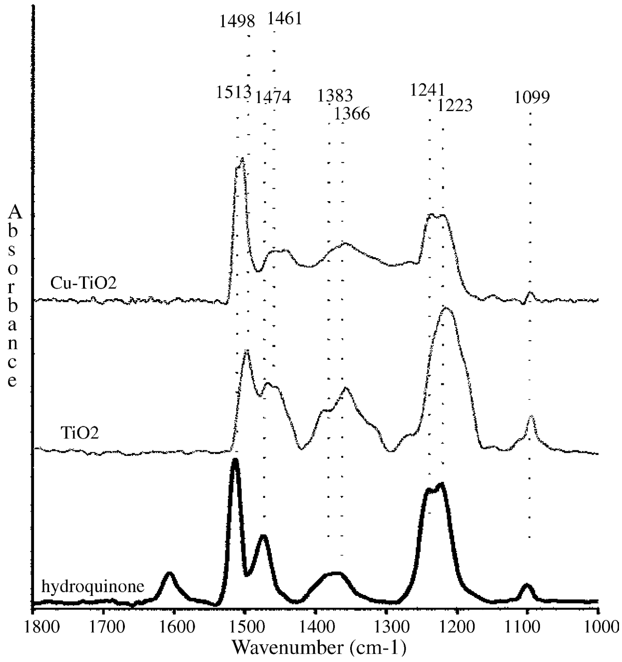


Fig. 5. IR spectra from hydroquinone interaction with TiO_2 and Cu-TiO_2.

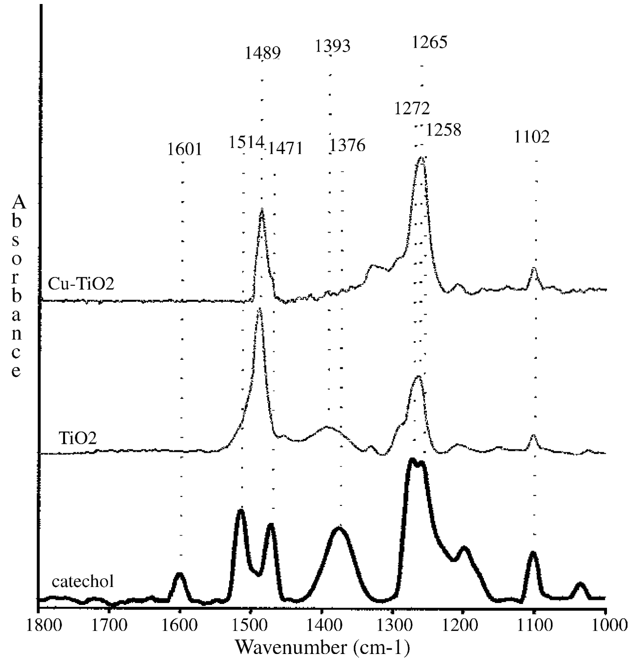
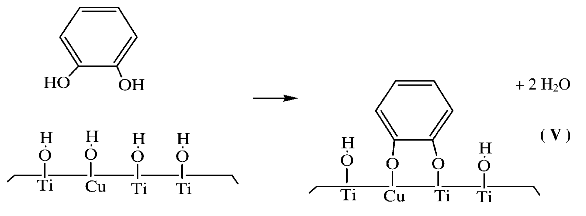


Fig. 6. IR spectra from catechol interaction with TiO_2 and Cu-TiO_2.

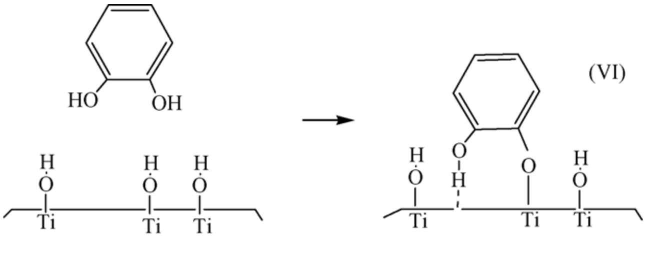
3.4. Catechol

Spectra from catechol interaction with the catalysts are quite different from the organic reference spectrum (Fig. 6). In both catalysts, bands at 1601, 1514 and 1471 cm^{-1} disappear while only one at 1489 cm^{-1} is visible As indicated above, these bands are attributed to aromatic ring νC–C vibrations. In Cu-TiO_2, the δOH vibration band from catechol (1376 cm^{-1}) disappears and νC–O (1272–1258 cm^{-1}) vibration band intensity is notably increased. However, in bare-TiO_2 the δOH vibration band intensity is lower than that from catechol reference spectrum, and appears shifted to higher wave numbers (1393 cm^{-1}).

Thus, Cu-TiO_2 interaction with catechol could be illustrated as follows:

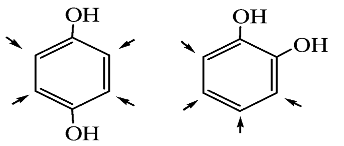


Nevertheless, in bare-TiO_2 the catecholate monodentate may be formed by

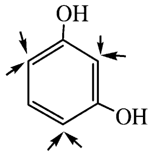


4. Discussion

As reported in the literature, for dihydroxybenzenes OH substitution in aromatic rings is favoured in *ortho* and *para* positions [27]. Hydroquinone and catechol show four activated positions for $^{\bullet}$OH radicals attack:



However, resorcinol has three doubly activated positions:



When any of these dihydroxybenzenes (structures II, IV–VI) establishes a covalent bond, the number of activated positions is reduced because Ti or Cu atoms would accept the electron pair. In addition to this, the relative activation of the free positions influences the catalytic activity and mechanism. The aromatic ring activation and deactivation due to this kind of interactions could be related to the different photocatalytic activities observed during the first minutes of reaction. These early reaction stages seem to determine the process rate.

For instance, when resorcinol structure II is formed with Cu-TiO_2, activating positions are reduced to three. This explains why resorcinol degradation by this catalyst is lower than that with bare-TiO_2, in which structure I is formed. The formation of structure I modifies the number of activating positions at a lower extent.

FTIR studies showed that hydroquinone interaction with both catalysts might be determined by structures III and IV. Even though, it has been indicated that structure III could be favoured in Cu-TiO_2, while structure IV in bare-TiO_2. This structure assignment is supported by the higher hydroquinone degradation obtained with Cu-TiO_2 than with bare-TiO_2. In structure III, there are still four activated positions, one more than three positions in resorcinol structure II. This is why hydroquinone degradation by Cu-TiO_2 is faster than that of resorcinol. In bare-TiO_2, the number of activating positions is larger for resorcinol than for hydroquinone.

Furthermore, FTIR studies from catechol interaction with Cu-TiO_2 suggested the formation of catecholate bidentate (structure V) that would prevent the activation of any position. Therefore, degradation with this catalyst is virtually nil. Catechol degradation rate reduction observed with this catalyst in the presence of H_2O_2 after the initial 20 min might also be attributed to this structure formation. However, structure VI was proposed with bare-TiO_2 since the activation of two positions would promote degradation.

We have not noticed a direct relationship between Cu(II) extraction from the catalyst surface and the achieved degradation. This is justified because photocatalytic behaviours of the different dihydroxybenzenes with $Cu^{2+} + H_2O_2$ solutions were quite similar. In other words, photocatalytic degradation depends on the organic–catalyst surface interaction type more than on dissolved Cu^{2+} ion concentration. Additionally, experiments in which less Cu(II) is extracted (with catechol) have shown lower degradation rates and the lowest aromatic ring activating structure has been determined. Otherwise, in experiments in which larger Cu(II) is extracted (with hydroquinone) have yield faster degradations and the more activating structures have been indicated.

5. Conclusions

In the present study, FTIR studies have made possible the correlation of different determined structures from the interaction of hydroquinone, catechol and resorcinol with the results obtained through photocatalytic degradation of these compounds.

As a concluding remark, when a covalent bond is formed between the organic to be degraded and the catalyst surface, the number of aromatic ring activating positions decreases and thus, the catalytic activity. On the contrary, if hydrogen bonds are established, faster photocatalytic degradations will be obtained.

The presence of Cu(II) atoms on the TiO_2 surface modifies the catalysts surfacial active centres, yielding different photocatalytic behaviour at the degradation of dihydroxybenzenes.

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