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Evidence for superoxide-radical anion, singlet oxygen and OH-radical intervention during the degradation of the lignin model compound (3-methoxy-4-hydroxyphenylmethylcarbinol)

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Abstract

Semiconductor slurries of TiO_2 were used during the photodegradation of the lignin model compound 3-methoxy-4-hydroxyphenylmethylcarbinol (from now on 3M-4HC). The TiO_2 P25 Degussa suspensions (1 mg/ml) of 3M-4HC were irradiated with a medium pressure mercury lamp in the pH range 3–8. The 3M-4HC (0.85 mM) disappeared within 40 min when using TiO_2 P25 Aeroxide Degussa and within 60 min with TiO_2 P25 Degussa as monitored by high pressure liquid chromatography (HPLC). The mineralization of 3M-4HC was observed to proceed within 120 and 180 min, respectively, indicating the existence of long-lived intermediates under light irradiation in solution. The addition of H_2O_2 accelerated the decomposition of 3M-4HC to almost completion within 30 min while the mineralization was observed to be complete only after 90 min. TiO_2 suspensions could be used repetitively as photocatalysts in the decomposition of 3M-4HC. The decomposition of 3M-4HC followed diffusion controlled pseudo first-order kinetics but the TOC seems to follow a mass transfer controlled process. No 3M-4HC decomposition was observed in the dark in the presence of TiO_2. The abatement of 3M-4HC was observed to be sensitive to the crystallographic structure, the crystal radius and the surface area (BET) of the TiO_2 used. The role of the oxygen singlet ($^1O_2$), of the superoxide anion radical $HO_2^{\bullet -}$ and of the OH-radical during the photocatalyzed degradation of 3M-4HC was elucidated by using sodium azide (NaN_3), benzoquinone (BQ) and OH-radical scavengers (methanol and *tert*-butanol), respectively. Evidence is presented for the intervention of these radical species produced on the TiO_2 surface under light irradiation during the 3M-4HC degradation.

Keywords: Photocatalysis of lignin model compounds; TiO_2 suspensions; Radical intermediates; Diffusion controlled processes; Mass transfer controlled processes

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1. Introduction

Lignin is a tri-dimensional amorphous polymer is amongst the most abundant biopolymers on earth, constituting 30% of the dry weight of soft woods and 20% of hardwoods [1]. In the last 20 years [2] degradation through oxidation of lignin has become a topic of interest as a way to discolor lignin and make useful in many applications [3]. Generally, chlorine compounds have been used as bleaching agents but chlorine-free agents like: O_2, O_3, H_2O_2 and UV-H_2O_2 are being recently explored since they are cheap and environmentally friendly working under mild conditions [4]. Photocatalysis using TiO_2 under light irradiation has been more recently used to partly degrade and discolor pulp lignin of different origins. This process uses the oxidative radicals produced by the semiconductor which attack the lignin inducing radical abatement of lignin [5–9]. The treatment of lignins by steam explosion with singlet oxygen was monitored by GC and UV-analyses [10,11].

The size, structure and complexity of the lignin polymer does not allow until now a detailed study of its degrada-

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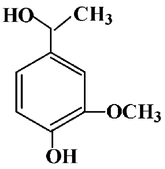
tion and discoloration. Therefore, many studies involve lignin model compounds to gain insight into the kinetics and mechanism of lignin degradation and discoloration. The model lignin compounds contain lignin isolated functional groups that constitute the lignin network. We have selected for this study the simple phenolic apocinol lignin model compound



3-Methoxy-4-hydroxy phenylmethyl carbinol

with the formula stated above and that is abbreviated in study as 3M-4HC.

The aim of this study is to find the solution parameters, the type of TiO_2, the UV-light intensity and the nature of some of the oxidative radicals participating in the abatement of 3M-4HC until mineralization is attained. The phenol compound chosen is representative and important in lignins which are made up of 20% phenolic compounds.

2. Experimental

2.1. Lignin model compound and chemicals

The 3-methoxy-4-hydroxyphenylmethylcarbinol was prepared by APIN Chemicals, 43rd Milton Park, Abingdon, Oxon, OX144RU, UK. All acid and bases, hydrogen peroxide, benzoquinone and sodium azide were from Fluka AG, Buchs, Switzerland and used as received. ZnO was obtained from Baker Chemical Industries and the TiO_2 P25 ($56\,m^2/g$) and TiO2 P25 Aeroxide ($90\,m^2/g$) were a gift from Degussa AG. De-ionized water was employed throughout this work.

2.2. Irradiation procedures and analyses

A 400 W medium pressure mercury lamp from Photochemical Reactors, Blounts Court, Reading, Berkshire RG49PA, UK was used to irradiate cylindrical Pyrex reactor (70 ml) with appropriate amounts of solutions. The integral radiant flux of the mercury lamp was measured with a power-meter (YSI Corp. Colorado, USA). The 3M-4HC absorption was followed in a Hewlett-Packard 38620 N-diode array spectrophotometer. The total organic carbon (TOC) was measured with a Shimadzu 5000 TOC analyzer. The disappearance of 3M-4HC was monitored in a Varian Corporation high pressure liquid chromatograph (HPLC) provided for with a 9065 diode. A Phenomenex C-18 inverse phase column was used and the gradient solution consisted of a buffer of ammonium acetate and methanol. The peroxide concentration of the solutions were measured using Merckoquant® paper from Merck Schweiz AG.

3. Results and discussion

3.1. Disappearance of 3M-4HC and TOC decrease under UV-light irradiation

Fig. 1a shows the disappearance of 3M-4HC as a function of time for different suspensions using TiO_2 Degussa P25 and ZnO in the dark and under light irradiation. Fig. 1 (trace 1) shows that in the dark no disappearance of 3M-4HC is observed due to the intermediates generated in solution precluding any 3M-4HC decomposition. UV-light irradiation of the TiO_2 was able to drive the oxidative reactions leading to 3M-4HC decomposition. It is seen from Fig. 1 (trace 2) that oxygen is not necessary as a conduction band electron scavenger to allow reactions between the TiO_2 and 3M-4HC leading to the degradation of the lignin compound. Ar is not an oxidant so that the direct reaction between the hole generated under light

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{cb} + h^+_{vb}) \quad (1)$$

$$TiO_2(e^-_{cb} + h^+_{vb}) + H_2O_{chem} \rightarrow H^+ + OH^\bullet + TiO_2(e^-_{cb}) \quad < 25ps \quad (2)$$

and the chemisorbed water on the TiO_2 generates the $OH^\bullet$ radicals that participate in a rapid interfacial charge transfer process [12]. The evidence for reaction (2) is supported by the following two experimental observations: (a) the pH decrease observed during 3M-4HC degradation reported in Fig. 1 (trace 2) from 4.0 to 3.3. This increase in H^+ concentration is equivalent to a seven-fold increase in the H^+ concentration in the suspension and (b) during degradation run of 3M-4HC experiments, methanol and *tert*-butanol were used as $OH^\bullet$ scavengers. The rate of degradation of 3M-4HC was considerably decreased as shown in Fig. 1c. Therefore it can be suggested that the $OH^\bullet$-radical participates in the 3M-4HC degradation along other oxidative radical species. The nature of the other species will be examined later in this study.

In reaction (2) the chemisorbed water may play an important role in the degradation of 3M-4HC generating the highly oxidative $OH^\bullet$ radicals which subsequently reacts with 3M-4HC. Recently Hashimoto and coworkers [13] reported the predominant involvement of the conduction band holes during the photocatalyzed oxidation of terephthalic acid on anatase.

Fig. 1 also shows that the performance of TiO_2 under light irradiation is a function of the O_2 dissolved in the suspension since the decomposition of 3M-4HC was kinetically faster and more efficient when solutions were purged before irradiation with O_2 than when air was used for this purpose (Fig. 1, trace 4). Trace 3 indicates that 3M-4HC is also decomposed by photolysis in the absence of TiO_2 during irradiation with a mercury lamp. The trace 5 in Fig. 1 shows that the semiconductor ZnO is effective in the decomposition of 3M-4HC under light but with a kinetics that is slower than the one found

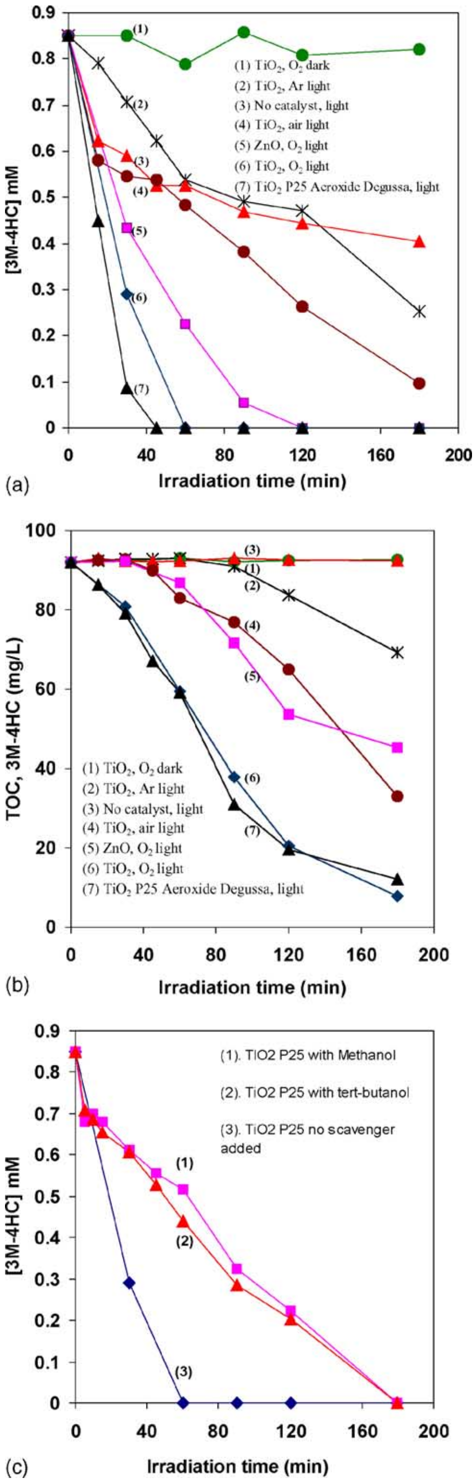


Fig. 1. (a) Decrease of the concentration of 3M-4HC as a function of irradiation time under a 400 W mercury lamp (150 mW/cm^2). Initial solution pH 4.0. The concentration of the semiconductor catalysts used was in all cases 1 mg/ml. Solutions were purged for 10 min before irradiation with the gas cited in the caption to this figure. TiO_2 in the caption refers to TiO_2 Degussa P25 when not specified otherwise. (b) Decrease of the TOC observed in 3M-4HC solutions as a function of irradiation time. Other experimental conditions as in Fig. 1a. (c) Decrease of 3M-4HC as a function of irradiation time in the presence of methanol and *tert*-butanol. Other experimental conditions as in Fig. 1a.

for TiO_2 Degussa P25 and TiO_2 Degussa Aeroxide P25. The superior performance of the Aeroxide compared to TiO_2 Degussa P25 may be due to his BET area of 90 m^2/g compared to 56 m^2/g of the P25 (see Section 2). Both Degussa TiO_2 powders are prepared by flame hydrolysis of $TiCl_4$.

The initial pH was varied between 3 and 8 for the run reported in Fig. 1a (trace 6). No variation was observed in the solution pH during the process leading to the disappearance of 3M-4HC. This shows that the TiO_2 Degussa P25 works as a buffer. The implication is that we do not have to adjust the initial pH for the degradation of 3M-4HC if we start the pre-treatment in the pH range 6–8 and couple this pre-treatment with a cheaper second stage bacterial treatment. An increase of the O_2 pressure beyond 1atm and up to 2 atm revealed no further increase was observed in the rate of 3M-4HC disappearance indicating that of 1.36×10^{-3} M O_2/l was an adequate concentration.

Fig. 1b shows the TOC decrease of 3M-4HC solutions as a function of light irradiation under the same experimental conditions used above in Fig. 1a. It is readily seen in Fig. 1b that the most effective TiO_2 samples in the decomposition of 3M-4HC (Degussa P25 and Degussa Aeroxide P25) are also the most efficient photocatalysts for the mineralization of 3M-4HC. No full mineralization was achieved within 3 h due to the generation of long lived intermediates precluding further mineralization under light irradiation. This study does not address the analyses and identification of the intermediates generated in solution which possibly involve the destruction of C–C single bonds requiring more time and more drastic oxidative conditions [14].

A common approach to enhance the charge separation during the TiO_2 photocatalysis to scavenge more efficiently the TiO_2 (e^-_{cb}) in reaction (2) using H_2O_2 as the oxidant in solution. Fig. 2a shows that 95% disappearance of 3M-4HC takes place within 30 min when H_2O_2 (10 mM) was added. The degradation kinetics of 3M-4HC can therefore be accelerated by a factor of two when TiO_2 Degussa P25 is used as a photocatalyst in the presence of H_2O_2 as compared with the results reported in Fig. 1 where H_2O_2 was not added to the solution(s). Fig. 2a also shows that H_2O_2 can oxidize 3M-4HC by itself within longer times than when TiO_2 Degussa P25 is added to the solution. The degradation kinetics of 3M-4HC reported in Fig. 2a shows that increasing the concentration of H_2O_2 enhances the 3M-4HC oxidation up to concentrations 10 mM. The shape of traces of 3M-4HC in Fig. 2a is seen to be different to the shape presented for Fig. 1 (trace 6) when using the same TiO_2 sample. This implies in the presence of H_2O_2 complex reactions take place on the TiO_2 surface. This will be examined later on when we address the TiO_2 surface generated intervention of $^1O_2$ and $HO_2^{\bullet-}$ radical species during the degradation of 3M-4HC.

Fig. 2b shows that in parallel to the disappearance of 3M-4HC (Fig. 2a) a TOC decrease takes place that is proportional to the concentration of H_2O_2 up to 10 mM. Above this concentration the photodegradation slows down since the prop-

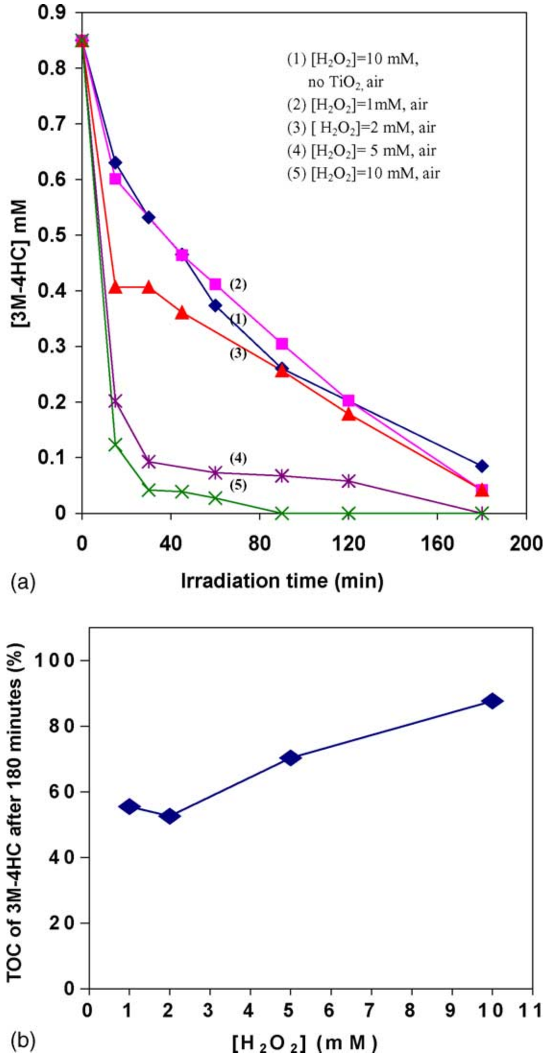


Fig. 2. (a) Decrease of the concentration of 3M-4HC as a function of H_2O_2 concentration under light of a 400 W mercury lamp (150 mW/cm^2). Initial solution pH 4.0. TiO_2 Degussa P25 was used in concentrations of 1 mg/ml. (b) Decrease of the TOC observed in 3M-4HC solutions as a function of irradiation time. Other experimental conditions used as in Fig. 2a.

agation step is hindered by the excess H_2O_2 scavenging the solution $OH^\bullet$ radicals

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HO_2^\bullet \tag{3}$$

3.2. Stable nature of the photocatalysis

Fig. 3a shows four repetitive cycles for the decrease in the HPLC signal of 3M-4HC as a function of irradiation time. TiO_2 Degussa P25 was used. Other experimental conditions used as in Fig. 1a. After each degradation run, the suspension was centrifuged to separate the TiO_2 from the solution and washed with water. Then 70 ml 3M-4HC was added before starting the next irradiation cycle.

Fig. 3b shows the spectrum of 3M-4HC reaching only up to 300 nm. The medium pressure mercury lamp used has an emission spectral output between λ = 230 and 440 nm. From the total output of the mercury lamp only 20% of the total emission intensity is comprised between 230 and 300 nm. Therefore, it can be estimated that of the light of the mercury lamp is adsorbed by TiO_2 in reaction (1) above, since the Pyrex Reactor Vessels used let paso light > 295 nm.

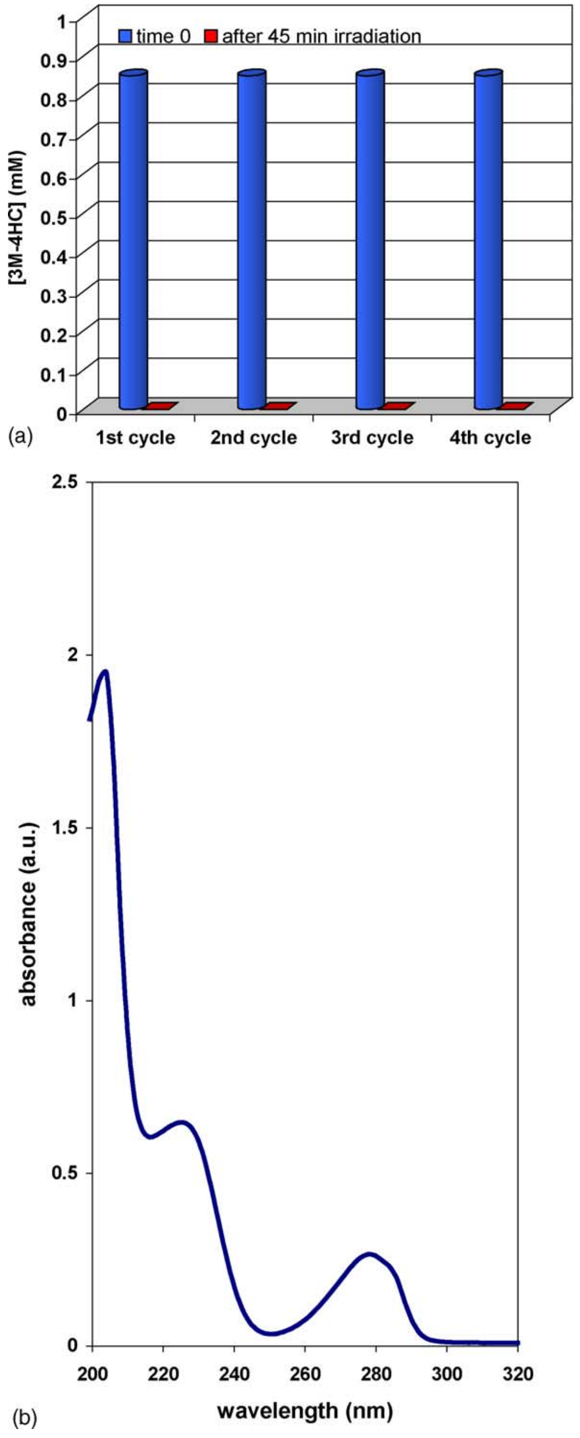


Fig. 3. (a) Repetitive cycles during the degradation of 3M-4HC. Other experimental conditions as in Fig. 1a. Solutions were purged with O_2 for 10 min before irradiation. (b) Optical absorption of 3M-4HC taken in a 1 cm silica cell.

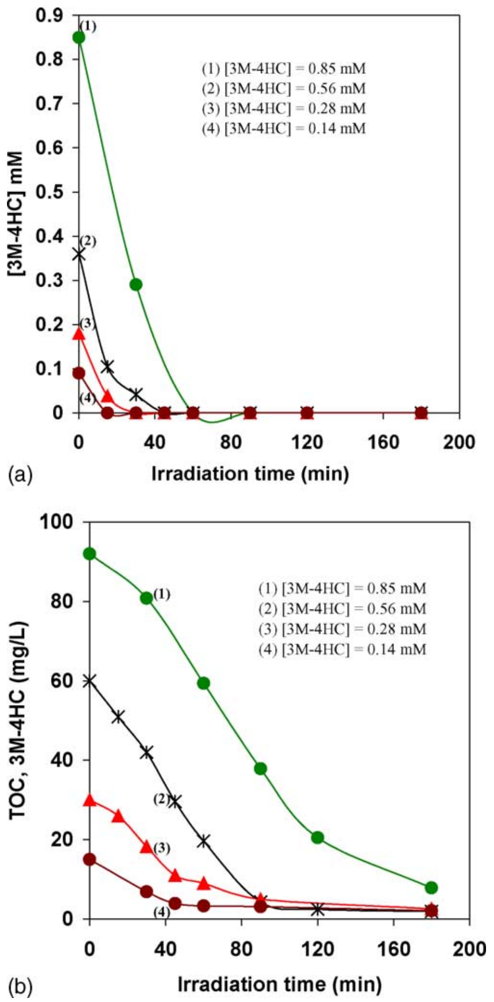


Fig. 4. (a) Decrease of the concentration of 3M-4HC as a function of 3M-4HC concentration under light of a 400 W mercury lamp (150 mW/cm^2). Initial solution pH 4.0. TiO_2 Degussa P25 was used in concentrations of 1 mg/ml. (b) TOC Decrease of 3M-4HC as a function of the initial concentration of model lignin compound. Initial pH 4, TiO_2 Degussa P25 used (1 mg/ml). Medium pressure mercury lamp. Solutions were purged with O_2 for 10 min before irradiation.

3.3. Dependence of the photodegradation rate on the initial 3M-4HC concentration

Fig. 4a presents the disappearance traces for four different concentrations of 3M-4HC. Pseudo-first order kinetics was observed for the decrease of the concentration of the reactant as a function of time. A higher concentration of the initial 3M-4HC is observed to have an inhibitory effect on the degradation of the model lignin compound. Diffusion controlled reaction between the reactant and the oxidative radicals produced in the solution seems to be going on in Fig. 4a.

Fig. 4b shows that for the three lowest TOC values the complete mineralization takes about 90 min and only for the highest one this time is increased by a factor of two. For the samples with the lowest TOC (Fig. 4b, traces 2–4) a mass transfer controlled process between the solution and the TiO_2 powder surface seems to take place since they need about the same time to undergo mineralization. This mass transfer is driven by the difference in 3M-4HC concentration between the bulk solution and the TiO_2 powder surface. That three different 3M-4HC concentrations need about the same time to mineralize is due to the fact that the mass transfer is directly proportional to the difference of the 3M-4HC concentration existing in the diffusion layer and the TiO_2 interface. This shows that neither in Fig. 4a nor in Fig. 4b the saturation of the TiO_2 catalyst reactive sites is attained. The 3M-4HC and the intermediates produced in solution were observed to be completely degraded.

3.4. Light intensity dependence of the photodegradation process

Fig. 5a shows the disappearance of 3M-4HC as a function of light intensity. It is readily seen that the rate of disappearance increases as the intensity of the applied light is increased. A very small light dose (22 mW/cm^2) is able to accelerate the photodegradation in a remarkable way. This shows that diffuse light can be employed in the degradation process with a low cost in the electrical energy. The results in Fig. 5a shows that saturation of the photocatalyst active sites was not reached when increasing the photon density. Fig. 5b also shows that the trend shown in Fig. 5a is valid for the TOC decrease as a function of applied light intensity. This results complement the observation presented in Fig. 1a for the decrease observed for 3M-4HC.

3.5. About the singlet oxygen $^1O_2$ and superoxide radical $HO_2^{\bullet -}$ roles during 3M-4HC photodegradation

Fig. 6a shows that added sodium azide and benzoquinone (BQ) in the dark produce no effect during the degradation of 3M-4HC in the presence of TiO_2 Degussa P25 at pH 3. Under light irradiation 71% of the initial 3M-4HC is left after 180 min irradiation with the mercury lamp. Under the same experimental conditions but with no benzoquinone (BQ), the disappearance of 3M-4HC was observed to be complete within 40 min. This shows that some of the $O_2^{\bullet -}$ present in the equilibrium

$$HO_2^{\bullet} \Leftrightarrow O_2^{\bullet -} + H^+ \qquad (4)$$

is consumed in the reaction

$$O_2^{\bullet -} + BQ \rightarrow BQ^{\bullet -} + O_2 \qquad (5)$$

and is not available to perform the oxidative radical attack on 3M-4HC[15]. Fig. 6b shows that 85% of the initial 3M-4HC is present after 180 min reaction for the same system shown in Fig. 6a for a suspension with an initial pH 6. Since the pK_a value of the equilibrium (4) is 4.7, the $O_2^{\bullet -}$ becomes the predominant species in solution at pH 6. From Fig. 6a and b, we can conclude that the main form of the superoxide radical intervening in the 3M-4HC degradation is $HO_2^{\bullet}$ and not $O_2^{\bullet -}$. These radicals have been reported to play an important role

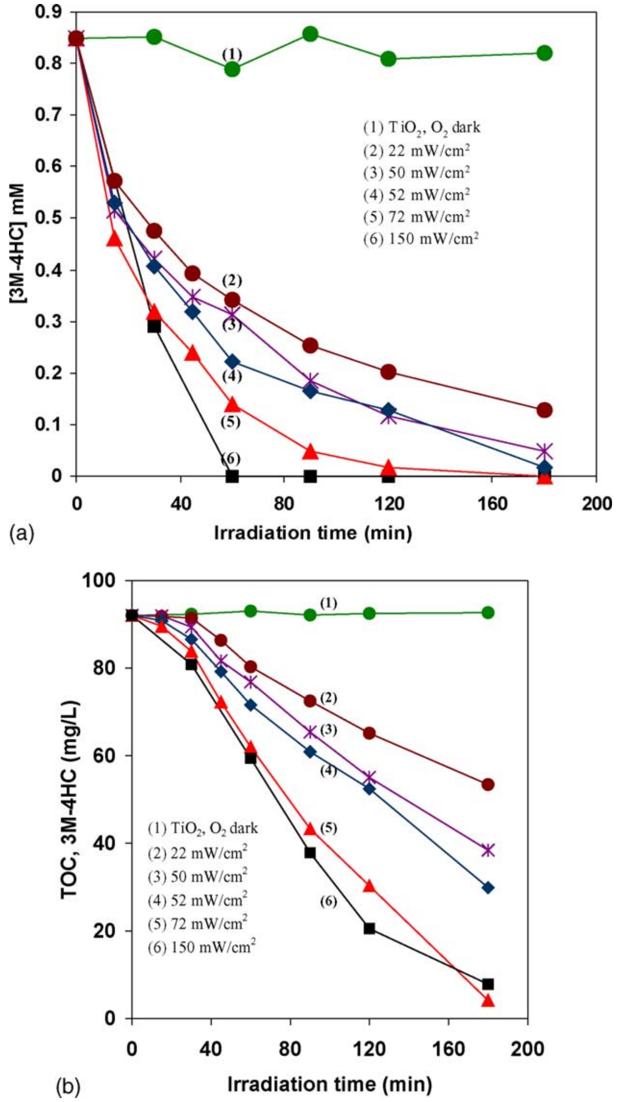


Fig. 5. (a) Effect of the light intensity on the photodegradation of 3M-4HC. Initial pH 4, TiO_2 Degussa P25 used (1 mg/ml). Medium pressure mercury lamp. Solutions were purged with O_2 for 10 min before irradiation. (b) Decrease of the TOC of 3M-4HC as a function of the applied light intensity. Other experimental conditions as in Fig. 5a.

during the ring opening of aromatic compounds [14]. In fact it is well known that one electron oxidation of phenols leads to the formation of phenoxyl radicals [16] which undergo ring-opening reactions in the presence of $O_2^{\bullet-}$.

Sodium azide (NaN_3) has been widely used to quench $^1O_2$ [17]. Fig. 6a shows that the disappearance of 3M-4HC is not influenced by the addition of NaN_3 at pH 3. The $^1O_2$ does not seem therefore to play a meaningful in the degradation of 3M-4HC at pH 3 since it does not preclude the degradation of the model lignin at this pH. Fig. 6b shows that the kinetics of 3M-4HC degradation is considerably longer upon addition of NaN_3. Since the added azide quenches the oxygen singlet, this result suggests the quenching of $^1O_2$ takes place after being generated from the precursor $O_2^{\bullet-}$ according to the reaction [4,14,17]

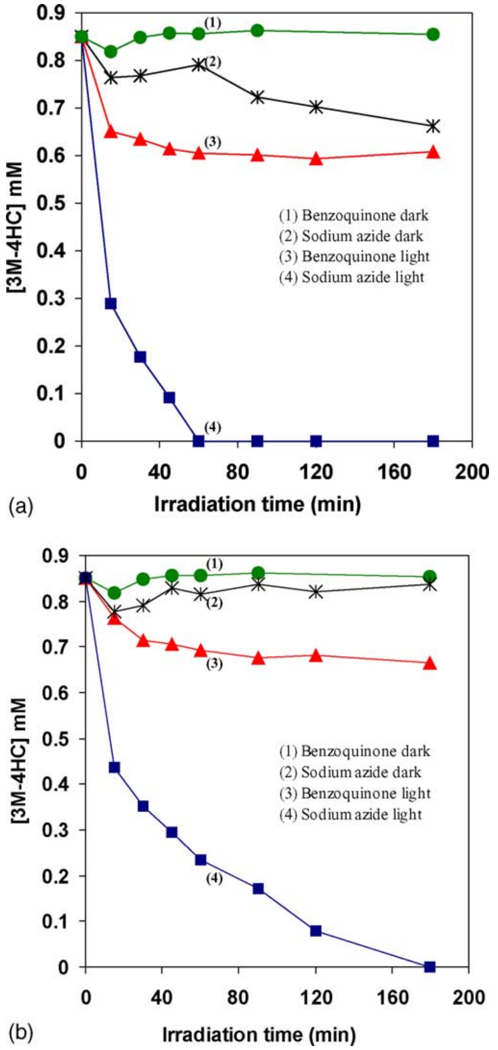


Fig. 6. (a) Disappearance of 3M-HC at pH 3 in the presence of sodium azide (0.25 mM) and benzoquinone (0.25 mM). TiO_2 Degussa P25 (1 mg/ml) is used under mercury lamp irradiation (150 mM/cm^2). (b) Disappearance of 3M-HC at pH 6 in the presence of sodium azide (0.25 mM) and benzoquinone (0.25 mM) TiO_2 Degussa P25 (1 mg/ml) is used under medium pressure mercury lamp irradiation (150 mW/cm^2).

$$2O_2^{\bullet-} + 2H^+ \rightarrow [\mathrm{HOO{-}OOH}] \rightarrow H_2O_2 + {}^1O_2 \qquad (6)$$

The standard free energy for reaction (6) of 37.5 kcal provides sufficient energy for the generation of singlet oxygen [18]. The possibility that singlet oxygen might be generated directly from triplet oxygen on the irradiated TiO_2 cannot be excluded, but we have no firm experimental evidence for this at the present time [19].

3.6. Disappearance of 3M-4HC as a function of the type of TiO_2 used

Fig. 7 shows the disappearance of 3M-4HC as a function of the type of TiO_2 used. It is readily seen that in the dark no 3M-4HC decomposition takes place when screening the

Table 1
Characteristics of the TiO_2 powders used in 3M-4HC degradation

TiO_2 type	Crystallographic phase	BET (m^2/g)	Crystal radius (nm)	Surface property
TR 92 huntsman	Rutile 94%	16	24	Al, Zr present
PC 10 millennium	Rutile 99%	10	70	Sulfate <0.3%
AMT 100 tayca	Anatase 95%	290	6	Chloride <0.3%
TKS 203 tayca	Anatase <90%	240	6	$Ti_3(PO_4)_4$ 5% neutral
TiO_2 degussa, P25	Anatase 80%, rutile 20%	56	20–30	SiO_2 0.2% Al_2O_3 0.3% Cl^- <0.3%
TiO_2 degussa, P25 aeroxide	Anatase 80%, rutile 20%	90	15–25	

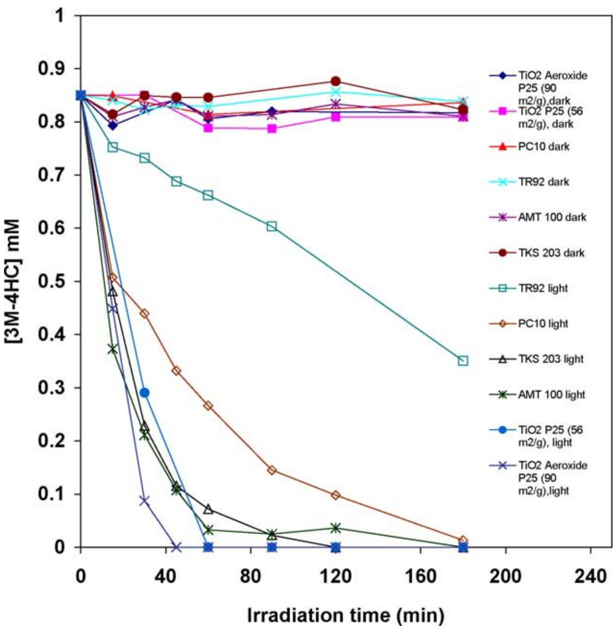


Fig. 7. Decrease of the concentration of 3M-4HC as a function of the TiO_2 used. The TiO_2 concentration was 1 mg/ml. Initial pH of the solution was 4.0 and a medium pressure mercury lamp is used (150 mw/cm^2). Solutions were purged for 10 min with O_2 before irradiation.

different titania samples. Under light irradiation the TR92 and PC10, the rutile samples were the less active samples photocatalyzing the disappearance of 3M-4HC. The anatase samples AMT 100 and TKS 203 showed a much higher pohotocatalytic activity in Fig. 7. The highest decomposition rate of 3M-4HC was attained with the TiO_2 samples having anatase and rutile in its structure. These samples are as noted as TiO_2 P25 having a different surface area of 56 and 90 m^2/g. The presence of two crystallographic phases seems to enhance the catalysis of the TiO_2 used during 3M-4HC decomposition. The catalytic performance of each of the TiO_2 samples cannot be ascribed to any single property of the TiO_2 used in Fig. 7. The main physical characteristics of the different samples of TiO_2 used are shown in Table 1.

4. Conclusions

This study reports basic information of the solution parameters affecting the photocatalytic degradation of a model lignin compound process. O_2 seems to play an important role during the observed degradation scavenging the TiO_2 conduction band electrons. Evidence is presented for the intervention of $^1O_2$, $HO_2^{\bullet -}$ and OH-radicals during the photocatalyzed degradation of 3M-4HC. The photodegradation of 3M-4HC was seen to proceed in the absence of O_2 upon irradiation of TiO_2 Degussa P25. This implies a rapid tunneling of the valence band hole from the semiconductor surface to the aqueous solution containing 3M-4HC. Different titania were used showing a different degradation activity on 3M-4HC. This is probably due to different BET areas, crystallographic phases and the density of the available surface traps available in the titania powders.

Acknowledgments

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