PERGAMON

Chemosphere 40 (2000) 115–124

CHEMOSPHERE

Photocatalytic degradation of lignin and lignin models, using titanium dioxide: the role of the hydroxyl radical

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Received 8 March 1999; accepted 7 June 1999

Abstract

The role of hydroxyl radicals on the degradation of lignins during a cellulosic pulp bleaching process including a photocatalytic stage, was assessed using peroxyformic acid lignins EL1 and REL1 and two phenolic biphenyl lignin models 1 and 2. The irradiations were performed in the absence of photocatalyst TiO_2 and H_2O_2 (condition a), in the presence of TiO_2 (condition b) and in the presence of H_2O_2 (condition c). The experiments were conducted in alkaline ($pH \approx 11$) aqueous ethanol solutions with oxygen bubbling. The relative phenolic content of the irradiated solutions, which is indicative of the involvement of hydroxyl radicals, was determined by ionization absorption spectroscopy. The results obtained show that the catalyzed reaction involves both degradation of the phenolate groups by electron transfer and hydroxylation of the lignin aromatic structure. Benzyl alcohol structural elements in sodium borohydride reduced lignin REL1 and compound 2 were also found as good trapping agents for the hydroxyl radicals. The degradation of EL1 was studied by measuring its fluorescence emission by comparison to the fluorescence of compound 2. The emission spectra indicate that some biphenyl phenolate anions in EL1 are reacting under UV/visible irradiation and some others, probably polyphenolic chromophores emitting less fluorescence, are formed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Lignin degradation; Hydroxyl radicals; Photocatalysis; Titanium dioxide

1. Introduction

Upon excitation with ultraviolet light, phenolic compounds in aerated aqueous solutions, undergo degradation yielding quinones, dimers and sometimes oligomers as major products (Mazelier et al, 1998). Lignin which is the second most abundant macromolecule in wood contains various phenolic and non-phenolic aromatic structural elements formed during its biosynthesis by dehydrogenative polymerization of coniferyl and synapyl alcohols. So, it is not surprising to note that photolysis of lignin conduces to similar degradation as observed for phenols, even though non-phenolic elements are absorbing the excitation light. The wavelength range required for lignin degradation is generally of lower energy (between 300 and 400 nm) than for phenols (<300 nm). This is due to the multifunctional character of lignin with some groups sensitizing the degradation of the phenolic elements (Neumann et al., 1986a, 1986b; Kringstad and Lin, 1970; Castellan et al., 1990). Excited α-carbonyl groups are able to abstract hydrogen from some lignin units,

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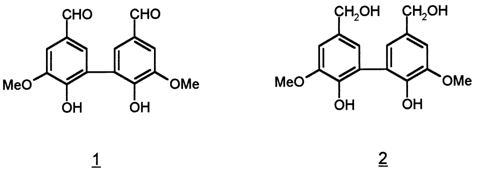
PII: S0045-6535(99)00269-6

preferentially phenolic hydrogen, initiating an oxidative chain reaction with the participation of ground-state oxygen, leading to the fragmentation and the formation of new chromophores such as quinones. It is known that the action of hydroxyl radicals can induce the formation of radical sites on a substrate, allowing further oxidation or disproportionation, the process being accelerated by oxygen (Gierer, 1997).

In a recent study (Perez et al., 1998a), we have used the semiconductor TiO_2 to enhance the photobleaching of pulps with UV/visible light. We proposed that lignin degradation in the presence of TiO_2 and light was due to the combined action of singlet oxygen, hydroxyl and superoxide radicals which are usually the principal reactive species generated in such a photocatalytic process in the presence of oxygen. The following equations summarize their formation under photocatalytic conditions (Serpone, 1997; Hoffman et al., 1995). $TiO_2(h^+)$ and $TiO_2(e^-)$ represent respectively, the electron-deficient and electron-rich parts in the structure of TiO_2, and S the lignin substrate.

$$\begin{aligned}
TiO_2 &\xrightarrow{h\nu} TiO_2(e^-/h^+)\\
TiO_2(h^+) + H_2O &\rightarrow TiO_2 + HO^{\cdot} + H^+\\
TiO_2(h^+) + S &\rightarrow TiO_2 + S^{+\cdot}\\
TiO_2(h^+) + OH^- &\rightarrow TiO_2 + HO^{\cdot}\\
TiO_2(e^-) + O_2 &\rightarrow TiO_2 + O_2^{-\cdot}\\
OH^- + O_2 &\rightarrow HO^{\cdot} + O_2^{-\cdot}\\
HO^{\cdot} + O_2^{-\cdot} &\rightarrow OH^- + {}^1O_2
\end{aligned}$$

In this communication, the role of hydroxyl radicals in the photocatalytic delignification process was approached using two soluble lignins. One, EL1, was obtained by peroxyformic acid pulping of *Eucalyptus grandis* wood and was previously well characterized by spectrometric methods (Perez et al., 1998b), the second one, REL1, was obtained from EL1 by the action of sodium borohydride which is known to reduce carbonyl group. The study was also extended to the phenol biphenyl model compounds 1 and 2 which mimic condensed residual lignin. Ionization UV/visible absorption and fluorescence emission spectroscopies were the two main techniques used (Scheme 1).



1 2

Scheme 1. Formulae of the studied biphenyl lignin model compounds.

2. Experimental

The degradation of the lignin samples EL1 and REL1 and of the lignin model compounds 1 and 2 was monitored at different reaction times under similar conditions to those used for the photobleaching of cellulosic pulps (photocatalysis at alkaline medium, pH = 11), using UV-visible radiation ($\lambda > 300$ nm) supplied by a 400 W medium pressure mercury lamp. The photochemical reactions were performed at 25°C in a cylindrical Pyrex glass reactor (5 cm diameter) equipped with a cooling jacket; it was positioned at 8.0 cm from the lamps. During the reaction, the medium was maintained under constant oxygen bubbling. The reactions were carried out on a solution of lignin or model (25 ml) in a mixture of ethanol and water (1 V/4 V) at a concentration of 0.25 mg ml^{-1}. Three conditions were used as: (a) with absence of TiO_2 and H_2O_2; (b) with presence of TiO_2 and absence of H_2O_2; (c) with presence of H_2O_2 and absence of TiO_2. For the experiments performed in the presence of titanium dioxide, a TiO_2 – substrate weight ratio equal to 1/50 was used, whereas for those in the presence of hydrogen peroxide, equimolar concentration of H_2O_2 and substrate was considered.

The lignin EL1, from *Eucalyptus grandis* wood, was obtained from the peroxyformic acid pulping spent liquor, by means of dissolution in sodium hydroxide solution (0.1 N) and precipitation in a solution of hydrochloric acid, after solvent evaporation. The precipitate, after centrifugation, was dried before use. The spectroscopic characterization of this lignin, detailed in the previous publication (Perez et al., 1998b), will be referred for the discussion. The lignin model dehydrodivanillin 1 was prepared by oxidative coupling of vanillin (Elbs and Lerch, 1916). Both the lignin REL1 and the compound 2 (1.5 g) were obtained from lignin EL1 and compound 1 respectively by action of sodium borohydride (1 g) in ethanol (100 ml) for four days at room temperature. Then the reaction mixture was acidified with dilute hydrochloric acid, the precipitate was washed with distilled water until neutrality, and then the material was dried in an oven at 40°C. UV absorption of the lignin and model compounds showed complete removal of the carbonyl chromophores.

Lignin degradation was monitored by size exclusion chromatography (SEC), using the samples obtained after photolysis in the presence of TiO_2, followed by solvent evaporation under vacuum at 45°C and dissolution in tetrahydrofuran (1 ml). The resulting solution (20 μl) was injected in a Merck–Hitachi HPLC equipped with four Shodex KF800 columns in series giving an exclusion limit between 1.5×10^3 and 4.0×10^5 Da. A Hach DR-4000U UV/visible spectrometer was also used to follow the reactions, measuring the variation of the absorbance at 280 nm for EL1, REL1 and compound 2 and that at 350 nm for compound 1. The phenolic content was evaluated by a differential absorption spectrometry, using a methodology proposed by Wexler (1964). Prior to analysis, two samples of the substrate were prepared at the same concentration by diluting 2 ml of the photolyzed solutions to 10 ml with HCl (0.1 N) and with NaOH (0.1 N), respectively. The phenolic hydroxyl group content in the sample was directly expressed as relative absorbance which were measured with the acidic solution placed in the reference beam.

The fluorescence spectra were recorded on a Hitachi F4500 fluorimeter using the non-corrected mode with the excitation and emission slits adjusted to 2.5 nm. The spectra were recorded for basic ($pH = 11$) and almost neutral ($pH = 6$) solutions with an absorbance adjusted around 0.1 at 280 nm.

3. Results and discussion

3.1. Irradiation of EL1 and REL1 lignins

The involvement of hydroxyl radicals in the lignin photodegradation process was approached by measuring the variation of the phenolic content of the sample determined by ionization absorption spectroscopy set up by Wexler (1964). The lignin degradation was induced by three different photochemical processes with: (a) photolysis of lignin by UV/visible light in alkaline solution ($pH = 11$) in the presence of oxygen, the light promoting the electron transfer from the phenolate anion to the oxygen molecule (Marcoccia et al., 1991); (b) photocatalyzed assistance by TiO_2 (Perez et al., 1998a); and (c) the benefit from species generated, by the photodecomposition of hydrogen peroxide, which is known to induce delignification (Tatsumi and Terashima, 1981).

The results of the irradiation of lignin EL1 are presented in Fig. 1.

The curve (a) indicates a sharp decrease of the phenolic content. It was not unexpected considering that the phenolic content of the lignin was high ($\approx 0.5/C_9$ unit (Perez et al., 1998b)) and that under direct photolysis the generation of hydroxyl radicals is not favored. Therefore, the oxidation of the phenol groups giving phenoxyl radicals appears to be the main channel of disappearance of these groups. On the other hand, one of the processes expected during the direct photolysis of lignins is the excitation of carbonyl groups, which can promote hydrogen abstraction, preferentially from free phenolic groups (Neumann et al., 1986a, 1986b), generating radical sites in the substrate, allowing the propagation of an oxidative chain with the participation of molecular oxygen (Scheme 2).

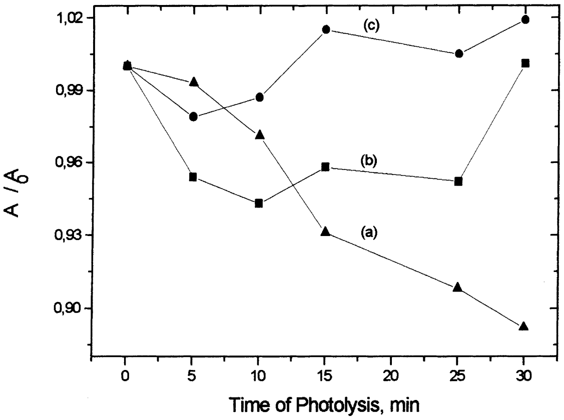
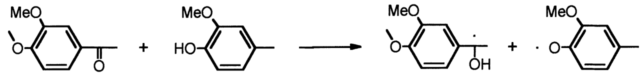


Fig. 1. Relative changes in the content of phenolic OH during the photochemical degradation of lignin under three different conditions: (a) direct photolysis; (b) photocatalysis (TiO_2/lignin = 1/50 w/w); (c) photolysis in the presence of H_2O_2 (H_2O_2/lignin = 1/1 mol/mol). The phenolic content is expressed in relative absorbance units given by ionization absorption measurements at 280 nm (Wexler, 1964).

This process might contribute to the observed reduction of the free phenolic groups content in lignin EL1 using the process (a). In other respect, the scission of β-O-4 structures could induce the formation of more free phenolic groups (Palm et al., 1992) but their content in EL1 was estimated approximately at $0.1/C_9$ units (Perez et al., 1998b) and so they cannot justify a significant increase of the phenolic content.

The behavior of lignin under the conditions (b) and (c) was found to be very different from that observed under direct photolysis (a). In such cases, a rapid initial decrease in the content of phenolic hydroxyl groups was observed, followed by a clear tendency of increasing, due to the incorporation of hydroxyl groups on aromatic rings, occurring by hydroxylation and/or demethoxylation (Gierer, 1997).

In contrast to the direct irradiation, the TiO_2 photocatalyzed reaction generates hydroxyl radicals ($^{\cdot}OH$) and anion superoxyde ($O_2^{-\cdot}$) as previously discussed in Section 1. The high reactivity of the hydroxyl radicals is well known (Klopfer, 1987; Steenken, 1987). This is not the case for the superoxide radicals, although they have a long lifetime when compared to the hydroxyl radicals, their reactivity is comparatively low (Gierer, 1997; Sawyer, 1988; Mattes and Farid, 1986). However, it has



Scheme 2. Formation of phenoxyl radicals by intermolecular abstraction of phenolic hydrogen by carbonyl groups.

been shown that the selectivity of the superoxide during the bleaching process is higher than hydroxyl radicals (Gierer, 1997). The initial decrease noted for curve (b) has to be attributed to the direct photolysis mechanism, due to the minor content of hydroxyl radicals photocatalytically generated in the beginning of the reaction. This is a consequence of the low quantity of photocatalyst, relative to the lignin mass (1/50), selected to reproduce the nearest as possible pulp photobleaching conditions (Perez et al., 1998a; Castellan et al., 1999). This low quantity of photocatalyst allowed the preservation of the cellulosic fibers after a photocatalyzed pulp bleaching stage (Perez et al., 1998a). In the initial stage of the reaction, the rate of consumption of phenolic groups is higher than the rate of incorporation of hydroxyl radicals into the aromatic rings. When a steady-state concentration of hydroxyl radicals is reached, the reactions induced by these radicals become more important and their involvement in the degradation process increases. Some of them are indicated in Scheme 3.

When the irradiation was performed in the presence of hydrogen peroxide (Fig. 1, curve (c)), which is an important source of hydroxyl radicals, a remarkable increase of the phenolic content was observed. Their formation by homolytic scission of H_2O_2 is probably not the main process due to the low absorption coefficient of hydrogen peroxide in the wavelength range employed in this study. Decomposition of hydrogen peroxide by transition metal Fe^{2+}, Cu^{2+} (Landucci and Sanyer, 1975) or Mn^{3+} (Abbot, 1991) by Fenton reaction appears to be a more productive and realistic source of hydroxyl radicals.

The behavior of the sodium borohydride reduced lignin REL1 under irradiation conditions (a) and (c) is very similar to the non-reduced lignin EL1 (Fig. 2). In contrast, the irradiation of REL1 in the presence of TiO_2 (condition (b)) indicates that the incorporation of hydroxyl group in the lignin polymer is less efficient. This might be attributed to the existence of a competitive reaction involving the hydroxyl radicals reacting with the new benzyl alcohol structural elements formed by reduction of the conjugated α-carbonyl groups of EL1 (Scheme 4). When the ketyl radical incorporates β–O–4 structural elements, cleavage of the β–O–4 bond can occur generating phenoxyl and phenacyl radicals (Palm et al., 1992). For other structural elements, the ketyl radical reverts to α-carbonyl derivative which does not contribute to the degradative pathway.

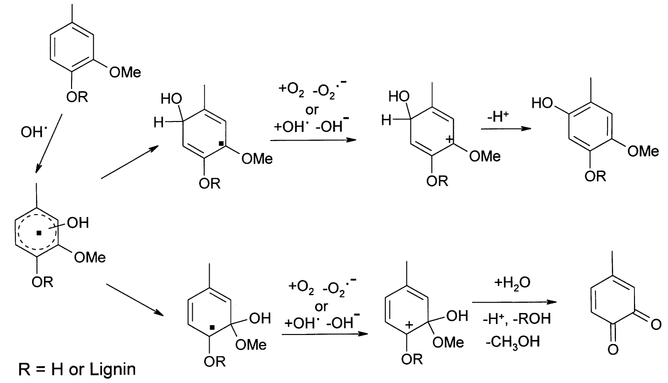
On the basis of knowledge of semiconductor photocatalyzed process (Villasenor and Mansilla, 1996), the expected trend is an increase of the phenolic content in the beginning of the reaction followed by breakdown of the aromatic structure of the lignin and its complete oxidation. This situation is reached when the ratio TiO_2/lignin equal to 1/5 is used as shown in Fig. 3. Both the similarity of the behavior observed for curves (b) and (c) in Fig. 1 and the results presented in Fig. 3 suggest that hydroxyl radicals play an important role during the TiO_2-photoassisted process, therefore we must take care about the amount of photocatalyst used for the bleaching.

An important fragmentation of the lignin structure during the photocatalytic process was monitored by size exclusion chromatography (SEC) (Fig. 4). A reduction of almost 50% in the average molecular weight of EL1 which was equal to 1.4 kD (Perez et al., 1998b), takes place after 90 min of irradiation.

The photocatalytic degradation noted by SEC is in contrast with the evolution of the absorbance measured at 280 nm for the lignin solution where an increase was observed (Fig. 5). This tendency suggests that the conjugation of the π system is extended, probably by oxidation of some lateral chains, giving stilbene or other conjugated chromophores.

3.2. Irradiation of lignin models 1 and 2

The involvement of hydroxyl radicals in the photocatalyzed degradation of lignin was also approached



Scheme 3. Reactions of hydroxyl radicals with lignin structural elements.

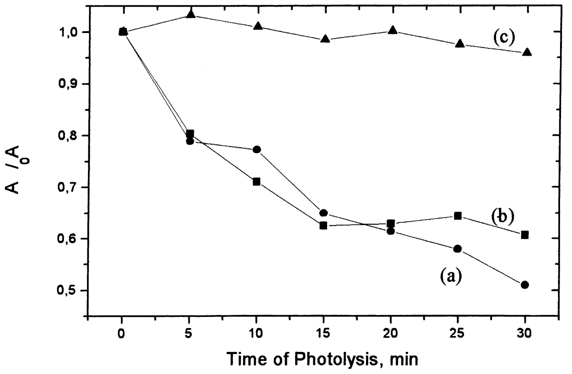
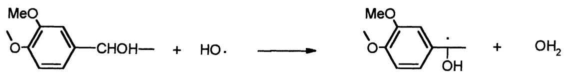


Fig. 2. Relative changes in the content of phenolic OH during the photochemical degradation of REL1: (a) direct photolysis; (b) photocatalysis (TiO_2/lignin = 1/50 w/w); (c) photolysis in the presence of H_2O_2 (see caption of Fig. 1).



Scheme 4. Reaction of hydroxyl radicals with benzyl alcohol structural lignin elements.

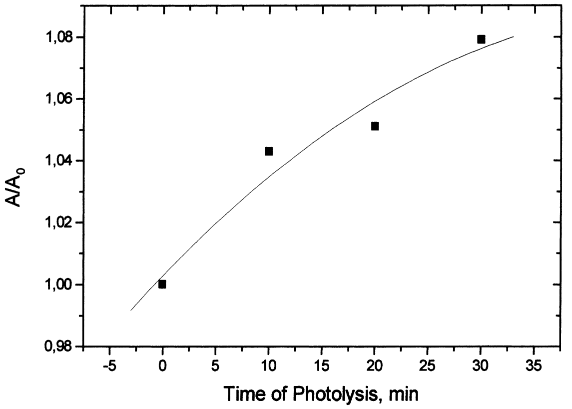


Fig. 3 . Relative changes in the content of phenolic OH during the photocatalytic degradation of lignin EL1 using larger quantity of TiO_2 (TiO_2/lignin = 1/5 w/w). The phenolic content is expressed in relative absorbance units given by ionization absorption measurements at 280 nm (Wexler, 1964).

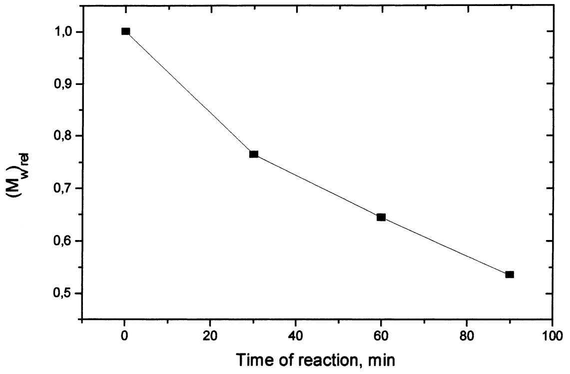


Fig. 4. Relative changes of average molecular weight number (Mw) of lignin EL1 solution versus irradiation time when irradiated with TiO_2. (See condition (b) of Fig. 1).

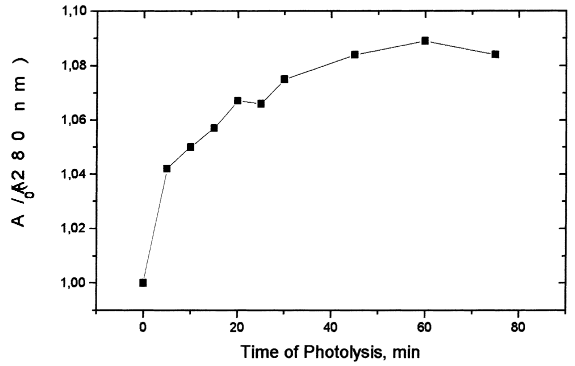


Fig. 5. Relative changes of the absorbance at 280 nm of lignin EL1 solution versus irradiation time when irradiated using the photocatalytic condition (b) of Fig. 1.

using the biphenyl lignin models 1 and 2 which might be considered as representative of phenolic condensed structures.

The relative changes in the content of phenolic hydroxyl groups during the photodegradation of the lignin models 1 and 2 are respectively presented in Figs. 6 and 7. Comparatively, the same trends as it was previously observed for the lignin EL1 and EL2 are seen for the biphenyl dimers 1 and 2. The decrease of the hydroxylation of the benzene structures noted in the photocatalyzed (b) process for REL1 is also observed for compound 2. This confirms, once again, the reactivity between the benzyl alcohol structural elements and hydroxyl radicals.

The comparative behavior of the lignin models and the lignin samples shows that the presence of conjugated carbonyl chromophores does not modify to a great extent the action of the hydroxyl radicals against the lignin polymer. Also, the electron transfer between the phenolate anion and the oxygen molecule seems to be the main mechanism operating in condition (a). This remains the observation made on high-yield pulps on the inefficiency of sodium borohydride treatment to stabilize the pulp against photodegradation (Heitner, 1993). In all these degradative processes, the conjugated carbonyl

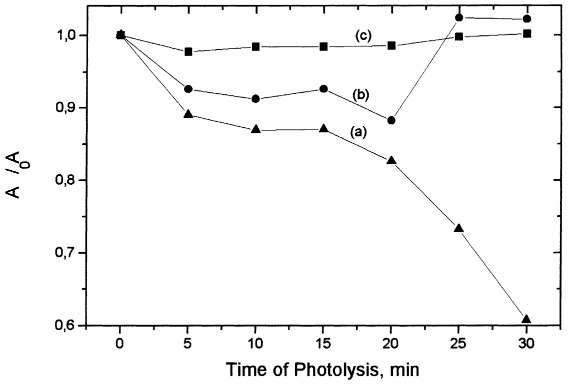


Fig. 6. Relative changes in the content of phenolic OH during the photochemical degradation of lignin model 1: (a) direct photolysis; (b) photocatalysis (TiO_2/lignin = 1/50 w/w); (c) photolysis in the presence of H_2O_2 (H_2O_2/lignin = 1/1 mol/mol). The phenolic content is expressed in relative absorbance units given by ionization absorption measurements at 350 nm (Wexler, 1964).

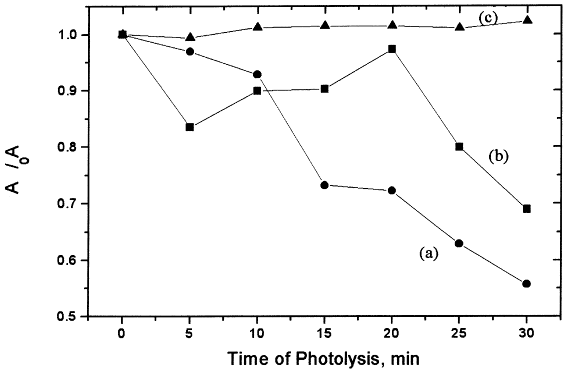


Fig. 7. Relative changes in the content of phenolic OH during the photochemical degradation of compound 2: (a) direct photolysis; (b) photocatalysis (TiO_2/lignin = 1/50 w/w); (c) photolysis in the presence of H_2O_2 (see caption of Fig. 1).

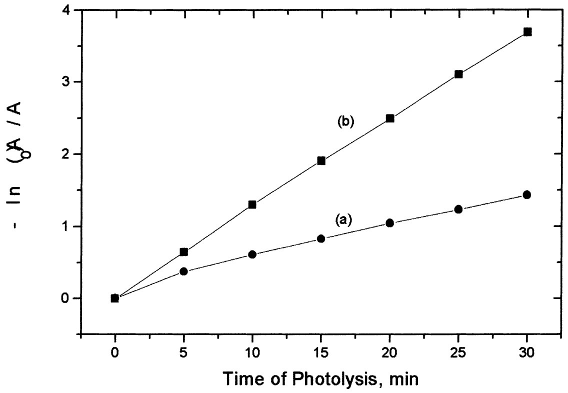


Fig. 8. Pseudo-first order kinetics for the degradation of dehydrodivanillin 1 monitored at 350 nm: (a) direct photolysis, without TiO_2, $k^I = 0.0458$ min^{-1}; (b) with the addition of TiO_2 (TiO_2/1 = 1/50 w/w), $k^I = 0.1227$ min^{-1}.

groups do not appear as the main actors of the breakdown of the lignin polymer.

In Fig. 8 are reported the pseudo-first order kinetics of the disappearance of dehydrodivanillin 1 monitored by the decrease of the absorbance at 350 nm using conditions (a) and (b). The photocatalytic process is at least three times more efficient to promote the degradation than the direct photolysis.

3.3. Study of the photodegradation of EL1 by fluorescence spectroscopy

Fluorescence spectroscopy has been proven to be a useful tool in the study of the photochemical behavior of pulps containing lignin and wood (Davidson et al., 1991; Castellan et al., 1992; Choudhury et al., 1992; Castellan and Davidson, 1994; Castellan et al., 1994a, 1994b). The luminescence of these materials has been mainly attributed to the lignin macromolecule. The emission spectra of the lignocellulosic materials in the solid state were found to be highly dependent on the wavelength of excitation, suggesting that the emission arises from different chromophores present in the lignin macromolecule (Davidson et al., 1991). In contrast, Lundquist et al. (1978, 1981) have shown that lignin samples in solution when excited in the wavelength range 250–350 nm gave very similar emission spectra. This is an indication that intramolecular energy transfer is occurring in solution and that the emitted light arises primarily from certain type of chromophores. It was found that reduction of carbonyl groups of lignin with sodium borohydride induced a strong increase of the fluorescence emission (Castellan et al., 1992). Quenching by carbonyl groups of the fluorescence emitted by the aromatic skeleton of lignin was assumed to be the main reason for this behavior (Castellan et al., 1992). Also, the relationships between the spatial arrangement of residual condensed lignin in the pulp and its luminescence properties were approached on non-phenolic biphenyl lignin models by comparing their luminescence emission and their structures in the crystalline state determined by X-rays (Guilardi-Ruggiero et al., 1997, 1999). The torsion angle in the biphenyl fluorophore appeared to be the main parameter governing the fluorescence emission in the solid and liquid states (Guilardi-Ruggiero et al., 1999). In this way, we decide to investigate by using fluorescence spectroscopy the behavior of the EL1 and REL1 lignins under the photobleaching conditions used in this study.

3.3.1. Fluorescence of EL1 and of compound 2 without irradiation

The fluorescence spectra obtained for neutral and alkaline aqueous acetonitrile solutions of EL1 and its sodium borohydride reduced derivative, REL1 using three excitation wavelengths, 290, 310 and 330 nm and two emission wavelengths, 390 and 430 nm. The excitation and emission fluorescence spectra of REL1 and EL1 were found very similar and for clarity only those of EL1 are presented in Fig. 9.

For a better understanding of the fluorescence properties of the EL1 and REL1 lignin, the fluorescence emission of compounds 1 and 2 were also studied, these compounds are considered representative of phenolic condensed conjugated lignin structure. As previously observed for other biphenyl derivatives, compound 1 was found non-fluorescent in our experimental conditions. This observation indicates that the fluorescence observed for EL1 was due to the non-carbonyl part of the lignin polymer. The fluorescence emission spectra of the lignin model 2 are reported in Fig. 10.

The excitation spectra monitored at 390 and 430 nm for the compound 2 are very similar and correspond to the absorption spectrum. A bathochromic shift (25 nm) is observed for the maximum of the first excitation band when the solution was brought to alkaline pH. Compound 2 displays two emission bands, the first one has a maximum situated around 350 nm and is not shifted when the medium was brought to alkaline pH. The maximum of the second band is shifted from 412 nm in neutral solution to 420 nm in alkaline pH (~11), this band originates from the phenolate anion. One can observe that the variation of the intensity of the phenolate emission band in alkaline medium follows the variation of the intensity of the absorption band with very similar intensity for excitation wavelengths equal to 290 and 330 nm.

Comparison of the fluorescence spectra of the lignin EL1 and the lignin model 2 indicates that the band at 343 nm observed for EL1 might be due to phenolic biphenyl fluorophore in their non-basic form as well as that emission in the range 400–500 nm is indicative of the existence of biphenyl phenolate fluorophores. Nevertheless, the non-similarity of both excitation and emission fluorescence spectra recorded for compound 2 and lignin EL1 shows that other chromophores in lignin EL1 are emitting in our experimental conditions. This was already observed for wood (Davidson et al., 1991).

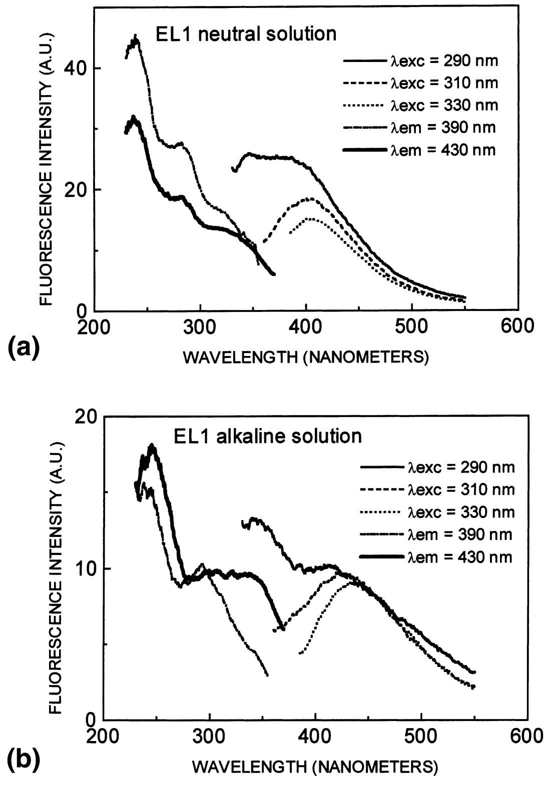


Fig. 9. Fluorescence spectra of lignin EL1 in aqueous acetonitrile solution (acetonitrile/water 1 V:1 V, temperature ≈300 K, fexc = fem 2.5 nm, absorbance at 280 nm ≈0.8, neutral solution: pH ≈ 6, alkaline solution pH ≈ 11).

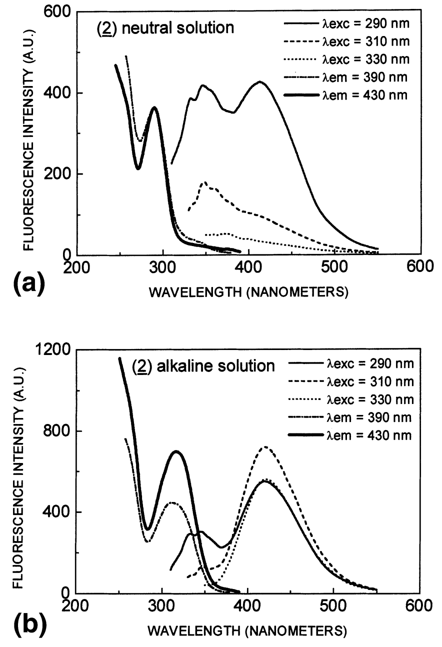


Fig. 10. Fluorescence spectra at room of the lignin model 2 in aqueous acetonitrile solution (acetonitrile 1 V/water 1 V, temperature ≈300 K, fexc = fem 2.5 nm, absorbance at 280 nm ≈0.8, neutral solution: pH ≈ 6, alkaline solution pH ≈ 11).

3.3.2. Fluorescence of EL1 after irradiation

The solutions of lignin EL1 were irradiated during 30 min using the conditions of Fig. 1(a)–(c). Then the solutions were diluted in a mixture of acetonitrile/water (1 V/1 V), the pH was adjusted to 11 and the fluorescence recorded using the same experimental conditions as for Fig. 9. The spectra are shown in Fig. 11.

A clear difference observed between the non-irradiated and the irradiated solutions spectra is the relative decrease of the intensity in the range 300–350 nm of the excitation spectra recorded for λ_{em} equal to 390 nm and 430 nm, especially for the latter. This region is characteristic of the biphenyl phenolate anion and this observation shows the reactivity of these anions under UV light exposure. Another observation, more or less related to the first one, is the difference in intensity for the range 400–500 nm between the emission recorded for λ_{exc} equal to 290 nm and 330 nm for the irradiated lignin solution compared to the non-irradiated one. In the non-irradiated sample EL1 (alkaline medium), the intensity of the emission (range 400–500 nm) is very similar when excited at 290 and 330 nm. The same phenomenon is observed for the biphenyl 2 solution (alkaline medium). The lower intensity emission observed when the excitation was set at 330 nm (alkaline medium) seems to be characteristic of the reactivity of the biphenyl phenolate anion. The same observation was done when biphenyl compound 2 solutions were irradiated using conditions (a)–(c) (spectra not shown). The fluorescence spectroscopy study performed in this work shows that chromophores, such as the biphenyl phenols, are destroyed and new fluorophores, less emitting, are formed during the photolysis, may be some polyphenolic compounds.

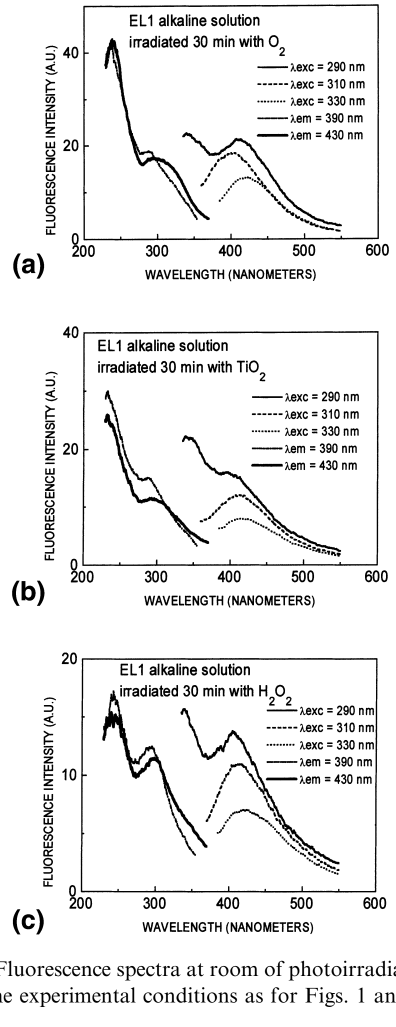


Fig. 11. Fluorescence spectra at room of photoirradiated lignin EL1 (same experimental conditions as for Figs. 1 and 9).

4. Conclusions

Although the overall mechanism of the photochemical bleaching process using TiO_2 as photocatalyst is not completely depicted using *Eucalyptus* peroxyformic acid soluble lignin in alkaline aqueous ethanol solution, some of the evidences are presented in this study. The hydroxylation of aromatic structures in lignin was found to occur during photochemical bleaching in the presence of TiO_2 or H_2O_2 which are known to generate hydroxyl radicals under UV/visible irradiation. The incorporation of hydroxyl groups to the benzene rings leads to the creation of radical sites allowing the action of both molecular oxygen and active species such the superoxide radicals. This results in the structural fragmentation of lignin. In contrast, the irradiation of the lignin without TiO_2 or H_2O_2 is dominated by the electron transfer between the phenolate anion and ground state oxygen leading to the breakdown of the phenolic units. This mechanism is operating in the beginning of the irradiation when the concentration of TiO_2 is low compared to lignin. The role of phenolic biphenyl units in the degradation of the studied lignin was revealed by comparison of the photochemistry of compound 1 and 2 in similar conditions as the lignin samples. Finally, the degradation of condensed structures, mimicked here by biphenyl units was assessed using fluorescence spectroscopy. This observation is highly connected with the effectiveness of the bleaching process once the presence of those structures in the residual lignin arising from acid process has been largely reported.

Acknowledgements

The authors are grateful to FAPEMIG for financial support, and to CAPES/ COFECUB (Project76/95) for travelling mission between Brazil and France and CNPq for grants. AC is very grateful to Conseil Regional d'Aquitaine and UE (FEDER Support) for help in the photobleaching project.

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