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Photodegradation of lignin from black liquor using a UV/TiO_2 system

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Abstract

An eco-friendly advanced oxidation processes (AOPs) have been developed for the treatment of lignin from alfalfa black liquor digestion. The method is based on the photodegradation of soluble lignin using TiO_2/UV photocatalytic technique. The photodegradation of the lignin black liquor have showed very interesting products such as vanillin and vanillic acid. The presence of these degradation products have been identified using GC–MS technique. The method is simple, effective and the resulted degradation compounds could be isolated and used as valuable industrial products.

Keywords: TiO_2; Degradation; GC–MS; Lignin

1. Introduction

The environmental pollution due to small and medium scale pulp and paper industries is multidimensional causing serious problems not only to the land mass fertility but also to the natural flora, fauna as well as the aquatic bodies. In order to manufacture good quality paper, the pulp and paper industry discards lignin as an unwanted constituent of wood and raw materials and therefore discharges a significant amount of effluent or wastewater containing lignin and other hazardous materials. Black liquor is one of the main by-products discarded as waste which contains lignin from 10 to 50% by weight. Lignin is highly resistant to microbial attack and major part of it escapes through conventional treatment processes into the water streams or land mass and thus results in severe environmental pollution. Several chemical and biological procedures are increasingly used in order to transform recalcitrant compounds into more biodegradable residues, some with success, but they are not widely implemented due to their high installation and operation costs [1,2].

Among the new oxidation methods or "advanced oxidation processes" (AOPs), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralisation of most of organic pollutants [3–5].

Recently, researchers have reported the degradation of the lignins induced by the interaction between lignins and singlet oxygen. They found that some lignins from steam explosion can undergo several modifications when irradiated in the presence of both oxygen and Rose Bengal [6–9]. Other works proposed photoelectrochemical methods for the degradation of lignin-sulphonate compounds [10].

In the present paper, it was attempted to optimise the conditions of the photocatalytic degradation by UV/TiO_2 system of lignin present in mill effluents from pulp and paper industries. We report for the first time the use of the UV light in the presence of TiO_2 for the oxidation of lignin from alkali alfaalfa digestion black liquor. The measure of its degradability by heterogeneous photocatalysis processes will permit us to bring of a solutions to the pollution problem of paper industries.

Furthermore, this work has been extended to identify some photocatalytic degradation products from of the lignin by GC–MS analysis. This phase of identification has been oriented mainly toward the aromatic derivative research that could present an interest for the chemical industry.

2. Experimental

2.1. Materials

Black liquor was supplied by a pulp and paper firm in Tunisia and used as received. Lignin was obtained by the

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precipitation of a black liquor sample (10 g) at pH $= 2$ with sulphuric acid followed by filtration and washing with acidic solution. Lignin solutions were prepared by dissolving the obtained solid in alkali solution using NaOH. The photocatalyst was titania Degussa P-25 (anatase/rutile $= 3 : 1$; surface area $= 50\,\mathrm{m^2\,g^{-1}}$, non-porous particles, mean size $=$ 30 nm).

2.2. Photoreactor and light source

Pyrex reactor open to air was utilised for all experiments. This reactor (1 l) was equipped with a plunging tube containing a Philips HPK 125 W lamp. This tube had a Pyrex cylindrical jacket in which water was circulated to avoid the heating of the solution. The intensity of the UV-radiation reaching the reactor ($\lambda > 290$). The intensity of the UV radiation reaching the reactor to deliver an efficient photonic flux (i.e. absorbable by titania) was measured using the ferrioxalate actinometry method and estimated to 6.67×10^{-7} einstein/s (mole of photons per second).

2.3. Procedure

The degradations were carried out at 293 K using 1000 ml of lignin solution and 1 g of TiO_2. The pH was adjusted using NaOH. The suspension was first stirred in the dark for 40 min before irradiation in photocatalysis experiment. This was sufficient to reach an equilibrated adsorption as deduced from earlier studies [11].

2.4. Analyses

Before analysis, the aqueous samples were filtered through 0.45 μm membrane filter to remove TiO_2 agglomerates. A "Jenway 6500" UV/Vis spectrophotometer recording the spectra over the 190–750 nm range was used for the determination of lignin concentration. A Beer–Lambert law was established to correlate the absorbency at 280 nm to lignin concentration. The chemical oxygen demand (COD) was determined using a Bioblock COD analyser based on the method of acidic oxidation by dichromate.

GC–MS analysis was performed with an HP model 5890 gas chromatograph, interfaced with an HP model 5872A mass selective detector. The analytical column connected to the system was an HP5MS capillary column (30 m × 0.32 mm internal diameter, 0.5 μm film thickness). The helium was used as the carrier gas with flow rate of 1 ml/min. The column temperature program was 80 °C (1 min); 80–280 °C ($7\,^{\circ}\mathrm{C\,min^{-1}}$, hold time: 5 min).

Sample from irradiated solution (80 ml) was acidified at pH $= 2$ by HCl (1 N) and extracted with ethylacetate (3 × 40 ml) then dried under nitrogen. BSTFA (100 μl) and TMCS (100 μl) were added to the organic extract. The solution was treated at 333 K under N_2 current for 5 h. The residue was redissolved in chloroform (1 ml) and analysed by GC–MS.

3. Results and discussion

3.1. Characterisation of lignin from black liquor

After the precipitation and purification from black liquor, the pure lignin were analysed by ICP as soluble solution at pH $= 9$. The results of ICP analysis are summarised in Table 1. We remark the presence of magnesium and calcium ions, the other metal ions were in negligible quantity. Thus, lignin solution was sufficiently pure to disregard the catalytic effect of metal ions.

The absorptivity at 280 nm of this black liquor lignin at pH $= 9$ was found to be $16.5\,\mathrm{l\,g^{-1}\,cm^{-1}}$ which is close to the value ($15.6\,\mathrm{l\,g^{-1}\,cm^{-1}}$) for a beech lignin previously reported [12]. The absorptivity was used to estimate the lignin concentration in aqueous solutions.

Finally, the characterisation of the lignin used in this work was completed by using the ^{13}C NMR (solid state) spectroscopy. With our sample, the spectrum presents four types of carbon that can be seen at $\delta = 148$, 132, 57 and 30 ppm. From these data, we can observe the presence of guaicyl and syringyl structures. These structures are both β-O-4 etherifided and non-etherifided. We noted the presence of cinnamaldehyd structures and C_5 condensed phenolic units. The ^1H NMR spectrum of soluble lignin in $_3DCOCD_3$ showed signals at $\delta = 1.05$, 1.45, 2.2, 2.45, 3.9, 4.27, 5.5, 6.8–7, 7.5 ppm.

3.2. Photocatalytic degradation of alkaline soluble lignin by TiO_2/UV

3.2.1. Evolution of lignin load in presence and in absence of TiO_2

Samples treated in photolysis or in photocatalysis contain 90 mg/l of lignin solutions at pH $= 8.2$. The irradiation of the solution was done by ultraviolet light in the absence of the catalyst in photolysis and in the presence of 1 g/l of TiO_2 in photocatalysis (Fig. 1). The irradiation in the absence of TiO_2 shows very little destruction of lignin containing solution from 91 to 88 mg/l corresponding to reduction of 3.3% in 420 min. Whereas, in the presence of TiO_2 the amount of degraded lignin increases to reach 56% in 420 min. The

Table 1
Chemical analyses of purified lignin (1000 mg/l lignin solution at pH $= 9$)

Measured features	Results
COT (mg/l)	330
pH	9
Ca (mg/l)	2
Mg (mg/l)	1.2
Na (g/l)	200
Fe (mg/l)	0.26
Al (mg/l)	2
Zn	Non-detectable
$SO_4{}^{2-}$ (mg/l)	95

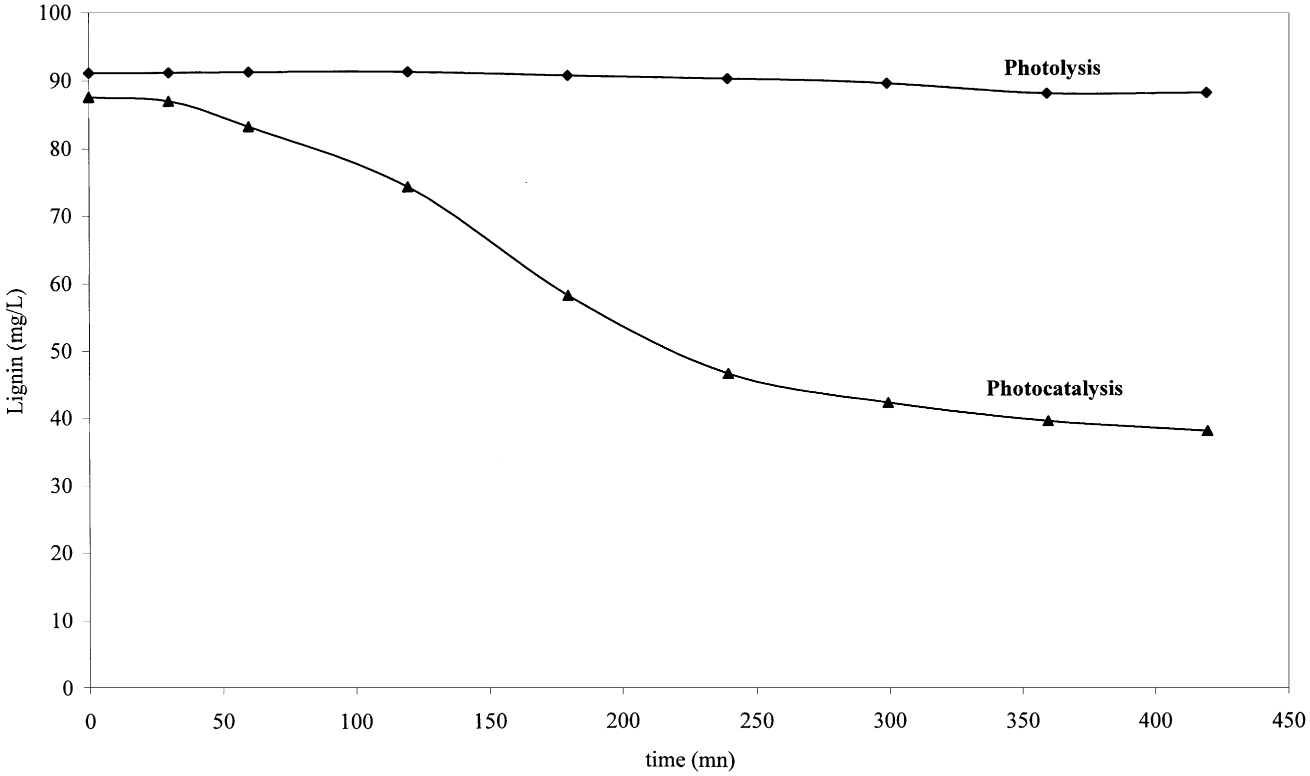

Fig. 1. Disappearance of Lignin by photochemistry and by photocatalysis under UV-irradiation.

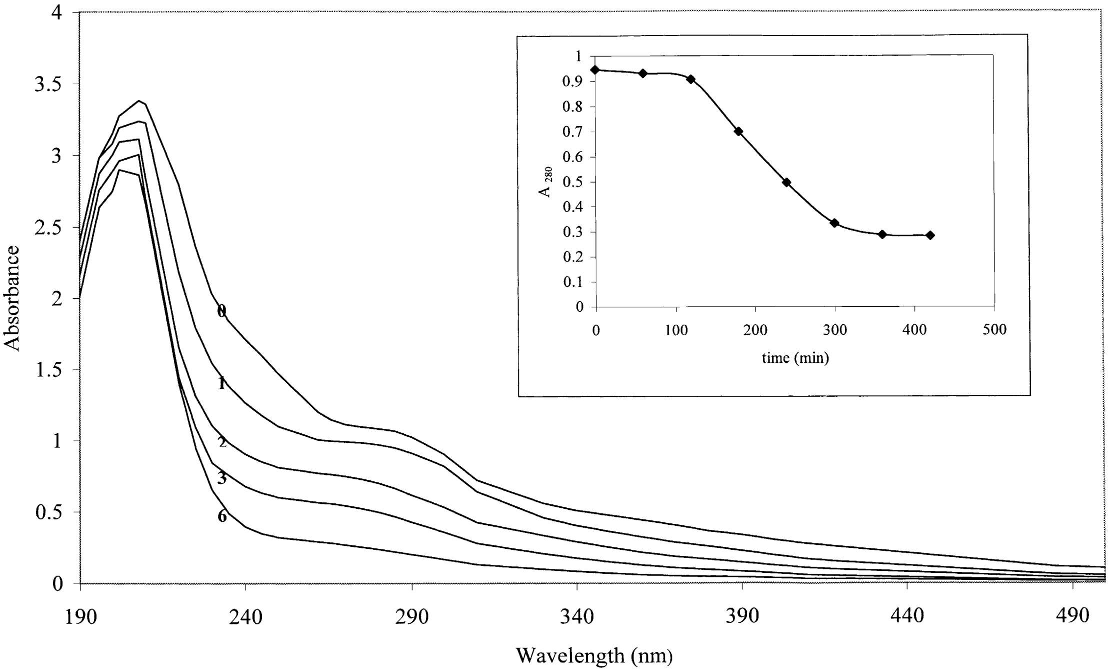

Fig. 2. Kinetics of the photocatalytic decolouration (OD = optical density) of lignin solution under light irradiation as a function of time. Traces taken at reaction times: 0, 1, 2, 3, 6 h. The insert represents the OD as a function of reaction time. Conditions: $C_0 = 90\,\mathrm{mg/l}$, $\mathrm{pH_{intial}} = 8.2$; $m(\mathrm{TiO_2}) = 1\,\mathrm{g}$; $V = 1\,\mathrm{l}$; $T = 30\,^{\circ}\mathrm{C}$.

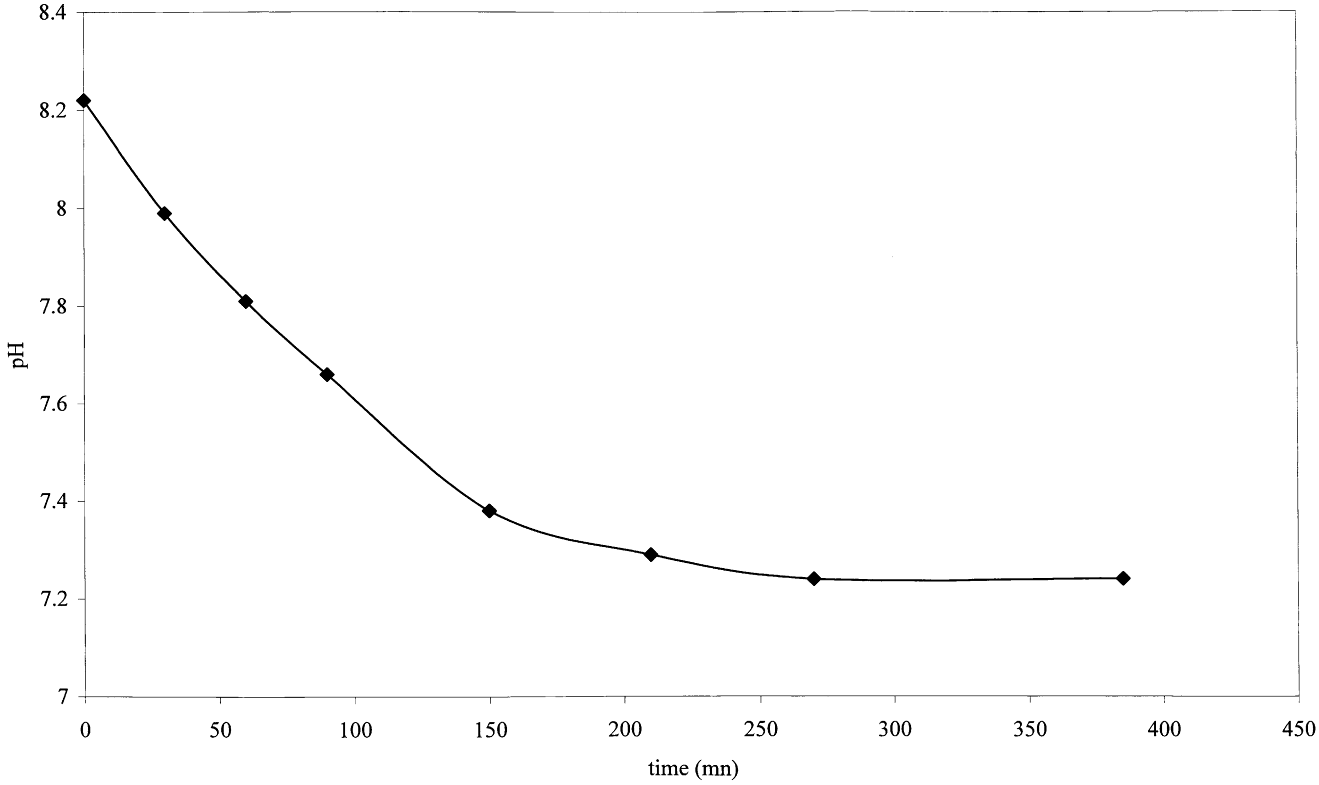

Fig. 3. Kinetics of pH changes during the photocatalytic lignin degradation. Conditions: $C_0 = 90\,\mathrm{mg/l}$, $m(\mathrm{TiO_2}) = 1\,\mathrm{g}$; $V = 1\,\mathrm{l}$; $T = 30\,^{\circ}\mathrm{C}$.

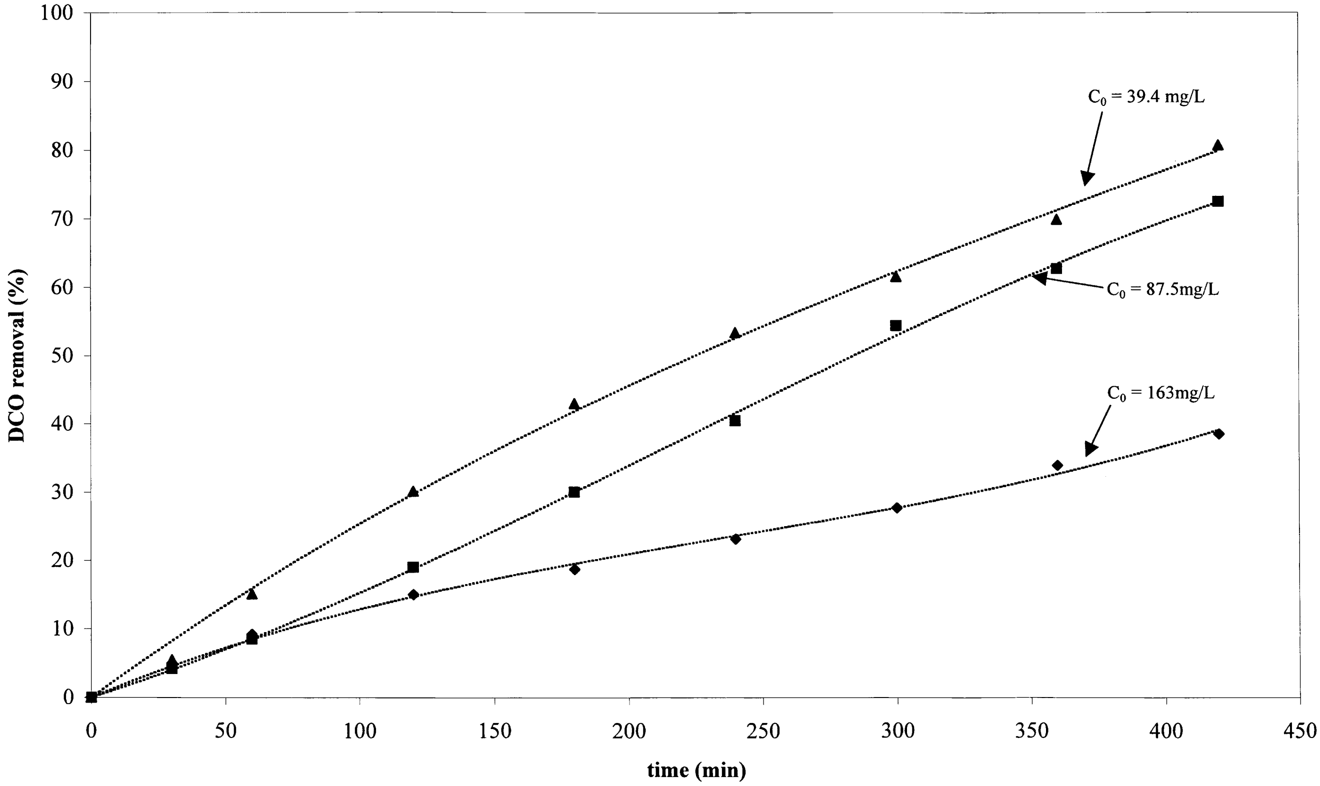

Fig. 4. Kinetics of COD removal for different initial lignin concentrations. Conditions: $m(\mathrm{TiO_2}) = 1\,\mathrm{g}$; $V = 1\,\mathrm{l}$; $T = 30\,^{\circ}\mathrm{C}$.

weak disappearance of the lignin in the absence of TiO_2 is assigned to the direct photolysis resulting in weak UV light absorbed by the lignin in the domain of the wave lengths transmitted by the Pyrex filter of the photo reactor ($290 < \lambda < 400$). A comparison of these two experiences shows that the direct photolysis of lignin is negligible to heterogeneous photocatalytic degradation.

3.2.2. *Decolouration of lignin solution*

Fig. 2 shows the decolouration of lignin solution at pH = 8.2 as followed by stopped-flow measurements. The decrease in the peak of lignin absorbency as a function of time (1, 2, 3 and 6 h) is summarised in this figure. The insert shows the reduction in the optical density with time from $OD_{280} = 0.94$ to 0.28 in 420 min. This gradual re-

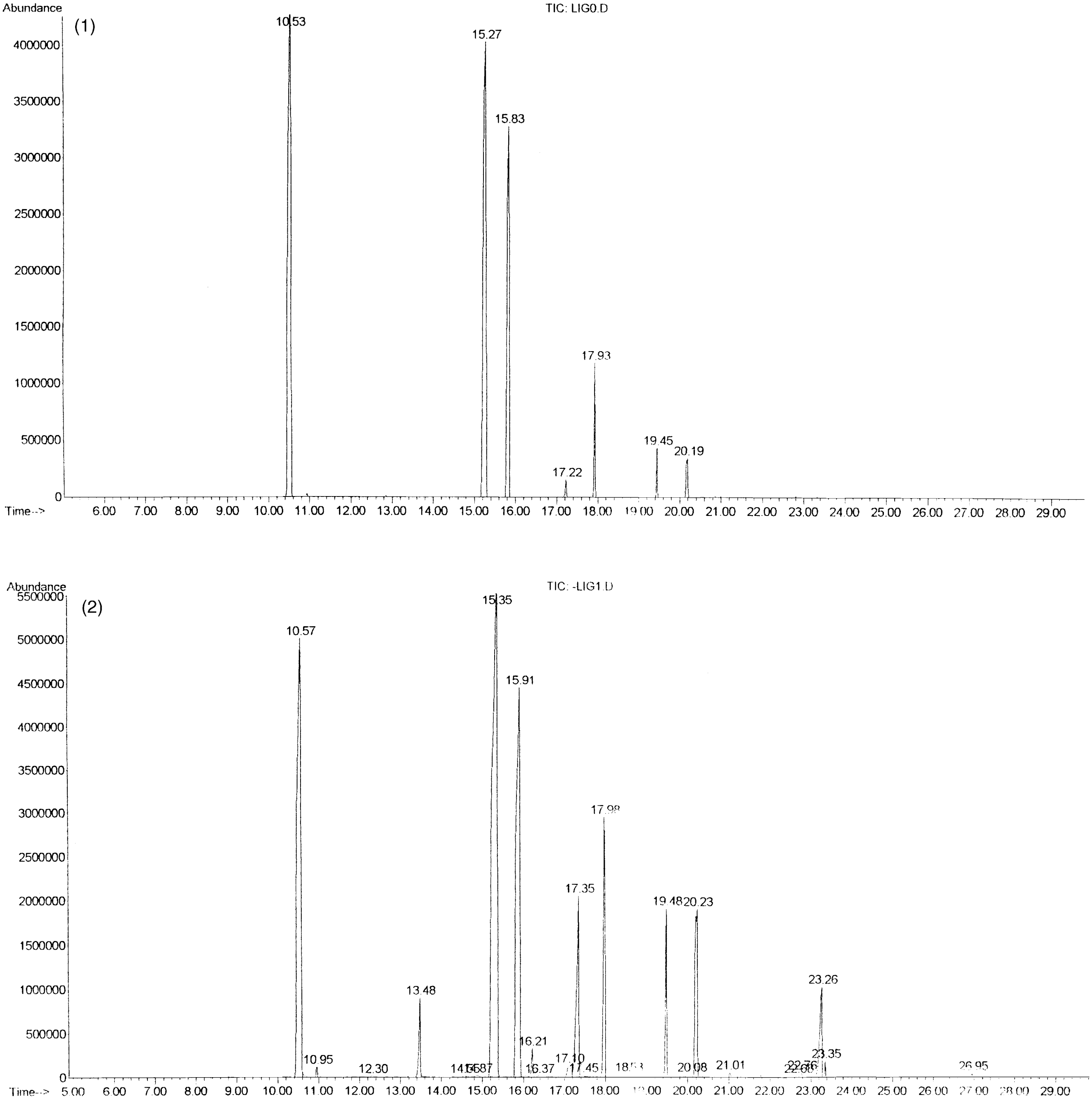

Fig. 5. Total ion gas chromatogram of ethylacetate-extractable products obtained from black liquor (chromatogram 1) and from irradiated solutions respectively for 30, 60 and 120 min (chromatograms 2, 3 and 4). The MS-identified compounds with respect of their retention time are the following: 4, 7: coniferylic alcohol; 10, 5: 3,3′-dihydroxy-4,4′dimethoxy-6-formyl-6′-methyl diphenymethane; 11, 06: syringaldehyde; 13.5: vanillin; 14, 9: 4-hydroxybenzoic acid; 16, 2: catechol; 17, 1: vanillic acid; 17, 3: 2-hydroxy benzyl alcohol; 17, 49: 3,4,5-trimethoxy benzaldehyde; 17, 54: *p*-coumaric acid; 18: 3-ethoxy-4-methoxy phenylpropanoic acid linked to 4-hydroxy-3-methoxy phenylethanol; 18, 65: diethyle phtalate; 20, 02: palmitic acid.

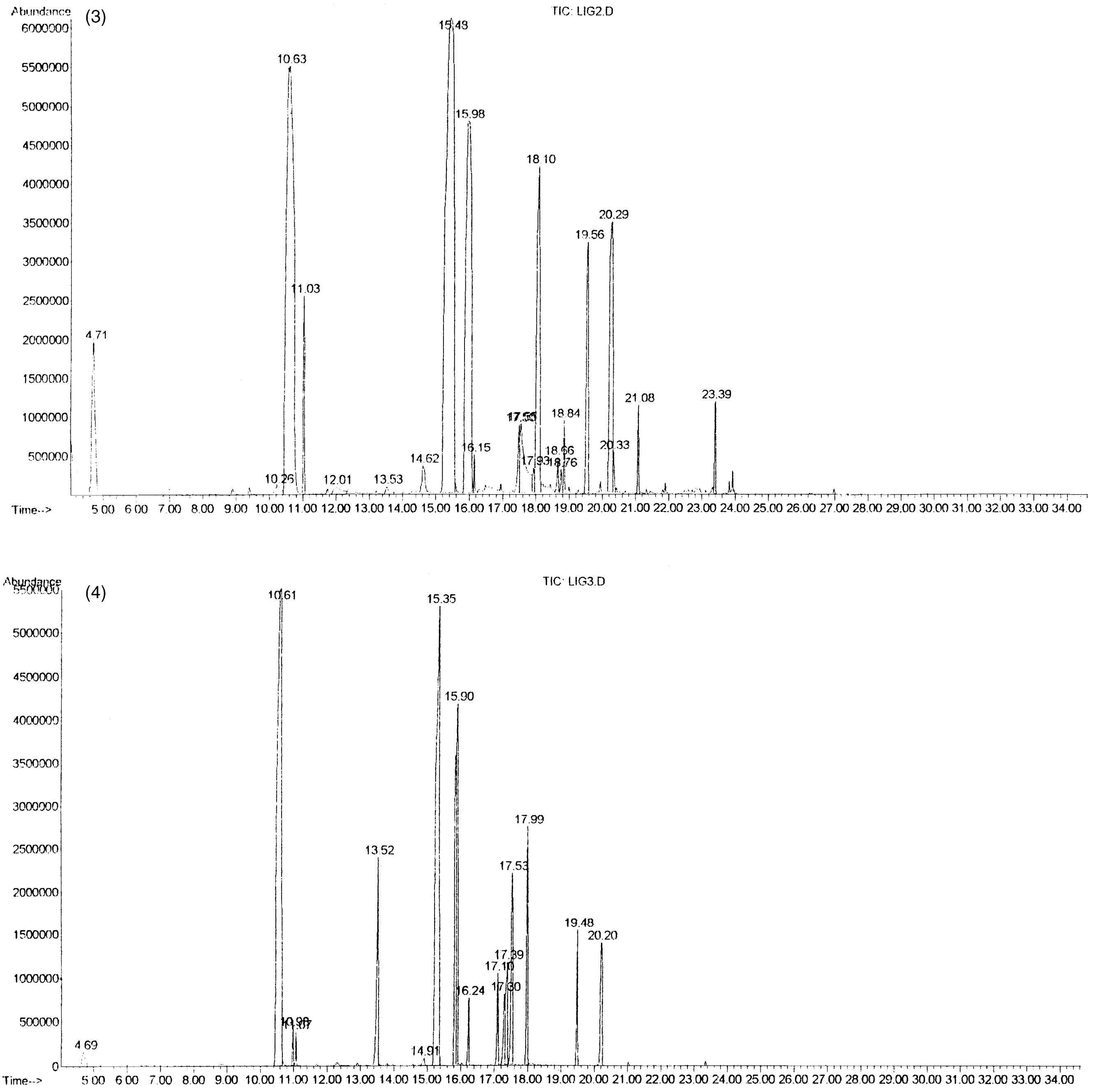

Fig. 5. (*Continued*).

duction of the intensity of the absorption proves that deterioration of chromophors groups of the lignin occurs. The absorbency at $\lambda = 280\,\text{nm}$ decreases after a phase of induction that probably corresponds to the depolymerisation phase of the lignin and the liberation of phenolic units. This one was followed by a decrease in the solution pH from 8.2 to 7.2 after 380 min of the UV irradiation (Fig. 3). This decrease in the pH was probably due to the enrichment of carboxylic acid groups during the photocatalytic oxidation.

3.2.3. *Catalytic quantum yield*

The catalytic quantum yield (ρ_0) is defined as the ratio of reaction rate r_0 to the photonic flux (φ) as the ratio of the number of molecules transformed per second to the number of incident efficient photons per second.

$$\rho_0 = \frac{r_0}{\varphi}$$

The efficient photonic flux has been determined by chemical actinometry, $\varphi = 6.67 \times 10^{-7}\,\text{einstein}\,\text{s}^{-1}$. The mean molecular weight of the lignin isolated from black liquor is in the order of 20×10^3 Da [13]. Since the initial speed of lignin degradation varies according to the initial concentration, we calculated the quantum yield corresponding to a large dilution: $r_0 = 5 \times 10^{13}$ molecules s^{-1} for an initial lignin concentration equal to 39.4 mg l^{-1}. The resulting initial photocatalytic quantum yield was equal to $\rho_0 = r_0/\varphi = 0.010\%$. This weak value of quantum yield can be explained mainly by the electron–hole recombination and also by the maximal theoretical quantity of photons that can be absorbed by TiO_2, either about 65% [14] because of the phenomena of reflection and scattering of the photons at the TiO_2 surface.

3.2.4. COD removal

Fig. 4 presents the chemical oxygen demand as a function of irradiation time for lignin initial concentrations of 163, 87.5 and 39.4 mg/l. The COD removal in the solution at lignin initial concentration of 193 mg/l decreases from 249.6 to 153.6 mg (O_2)/l with a capacity of 38% in 420 min. Whereas for the same reaction time, the COD removal reaches 72% for the initial lignin concentration of 87.5 mg/l. The COD decreases from 107.52 mg (O_2)/l to 29.44 mg (O_2)/l. The COD removal becomes higher (about 81%) for the lignin initial concentration of 39.4 mg/l. From these results, we note that the COD removal by photocatalytic degradation of the lignin solution depends strongly on the initial concentration of the substrate. Thus effective degradation could be achieved when lignin is used at weak concentrations. When the initial lignin concentration becomes higher, it will have an inhibitory effect on the photodegradation. This phenomena can be explained by the increase of incidental photonic flux irradiating the catalyst in dilute lignin solution. Thus the rate of hydroxyl radical $OH^{\bullet}$ and superoxyl $O_2^{\bullet -}$ production increases, which would allow the degradation to be faster [15].

3.3. Identification of the photocatalytic degradation products of the lignin solutions using GC–MS

3.3.1. CPG analysis of irradiated solution

After having studied the reactivity in heterogeneous photocatalysis of the lignin in alkaline solution, we tried to identify the products of photocatalytic degradation of the lignin. The identification was carried out using (GC–MS). This identification has been oriented mainly towards the aromatic derivatives that could present an interest to the chemical industry. The catalytic photodegradation of lignin was studied using optimum parameters, determined previously by Ben Amor et al. [16]. This experiment was achieved in the conditions that permit a partial degradation of the lignin. Thus we have used an important initial concentration in lignin (1.5 g/l) with TiO_2 concentration equal to 1 g/l, and the pH was maintained at 9. In the aim of identifying the initially present soluble derivatives in the black liquor, the ethyl acetate extract of the filtrate after lignin precipitation from fresh black liquor has been analysed, and results obtained are shown in Fig. 5 (chromatogram 1). Then, we chose to analyse the ethyl acetate extract of the filtrate of the of lignin solutions, irradiated for 30, 60 and 120 min (Fig. 5) (chromatograms 2, 3 and 4). The CPG analysis shows that intensities of some initial peaks in the black liquor increase during the photocatalytic reaction. Other peaks appear after 30 and 60 min of irradiation. This confirms that the photocatalytic reaction has been occurred and that new products were formed. Comparing the four chromatograms we noted that during the photocatalytic degradation of the lignin, the newly formed compounds were transformed in to more oxidised aromatic compounds.

Table 2
Main ions and relative abundances (%) obtained for lignin black liquor photodegradation by the UV/TiO_2 system identified by GC–MS technique (TMS derivatives)

Compound	Main ions (*m*/*z*) (% abundance)
3-(4-Hydroxy-3-methoxyphenyl)prop-2-ene-1-ol (coniferylic alcohol)	323 ($[M–H]^{+\bullet}$, weak); 295 (26); 207 (100); 191 (8); 73 (44)
3,3′-Dihydroxy-4,4′dimethoxy-6-formyl-6′-methyl diphenymethane	443 ($[M–3H]^{+\bullet}$, 5); 355 (10); 281 (21); 267 (17); 221 (39,7); 147 (40,8); 73 (100)
4-Hydroxy-3,5-dimethoxy benzaldehyde (syringaldehyde)	254 ($M^{+\bullet}$, 76); 239 (100); 196 (13); 112 (11); 73 (75); 45 (30)
4-Hydroxy-3-methoxy benzaldehyde (vanillin).	224 ($M^{+\bullet}$, 27,6); 209 (40,8); 194 (100); 73 (25)
4-Hydroxybenzoic acid	282 ($M^{+\bullet}$, 16); 267 (100); 238 (13); 223 (81,3); 208 (12); 193 (81,3); 73 (40)
Catechol	254 ($M^{+\bullet}$, 29,7); 239 (40,5); 224 (100); 193 (5,4); 182 (16,2)
4-Hydroxy-3-mtehoxy benzoic acid (vanillic acid)	312 ($M^{+\bullet}$, 62); 297 (100); 282 (27); 267 (70); 253 (43); 223 (61); 193 (26,3); 126 (30); 73 (73,7)
2-Hydroxy benzyl alcohol	268 ($M^{+\bullet}$, 56); 253 (68); 238 (93); 223 (100); 73 (66); 43 (34)
3,4,5-Trimethoxy benzaldehyde	196 ($M^{+\bullet}$, 53); 181 (100); 153 (13)
4-Hydroxycinnamic acid (*p*-coumaric acid)	308 ($M^{+\bullet}$, 33); 293 (43,4); 249 (24); 219 (64,5); 147 (7,9); 73 (100)
3-Ethoxy-4-methoxy phenylpropanoic acid linked to 4-hydroxy-3-methoxy phenylethanol	443 ($M^{+\bullet}$); 401 (52); 295 (12); 281 (35); 207 (100); 192 (10); 181 (35); 73 (98)
1,2-Dibenzoate of diethyle (diethyle phtalate)	223 ($M^{+\bullet}$, 8); 149 (100); 57 (34,6)
Hexadecanoic acid (palmitic acid)	256($M^{+\bullet}$, 39); 129 (40); 73 (100); 60 (74); 43 (97)

3.3.2. MS identification of products from lignin degradation in irradiated solution

According to the GC–MS spectra, we could identify some monomers of the lignin as the coniferylic alcohol and oxidised monomers as the syringaldehyde, vanillic acid and the *p*-coumaric acid (Table 2). Table 2 presents these compounds classified by their characteristic fragments and their relative intensities. The fragmentation obtained is identical to that reported for these compounds in the literature [17]. These compounds correspond to the oxidisation of the sinapylic, coniferylic and coumarylic alcohols. The peak at retention time 10.5 min was identified as the 3,3′-dihydroxy-4,4′-dimethoxy-6-formyl-6′-methyl-biphenylmethane. The presence of diphénylmethane in lignin residues of the Kraft process has been reported [18]. The peak at 18 min was identified as the ester of 4-hydroxy-3-methoxyphenylethanol and 3-ethoxy-4-methoxy phenylpropanoic acid. This linked compound shows in its spectrum a weak molecular ions at $m/z = 443$ and characteristic ion peaks ions at *m*/*z* 207 (base peak) and 192 resulting from McLafferty rearrangement typical of β-phenyl ethyl esters [19]. On the other hand, we found that the best yield in vanillin and in vanillic acid is obtained after 2 h of irradiation while the best yield in 4-hydroxy-3,5-dimethoxy benzaldehyde and in 3,4,5 trimethoxy benzaldehyde is achieved after 1 h of photodegradation. An aldehydic compounds of this type could interest the industry of the aromas and perfumes. Therefore this survey would deserve to be refined by optimisation of the conditions encouraging the quantitative and selective formation of some products such as vanillin and vanillic acid.

4. Conclusion

Lignin from alfalfa black liquor could be successfully decolourised and degraded by titania-based photocatalysis at room temperature. The analysis of the residue showed the presence of some lignin derivatives, such as vanilline, coniferylic alcohol, highly oxidised phenols like syringaldehyde, vanillic acid and the *p*-coumaric acid. We also showed the presence of palmitic acid. Finally, we observed the formation of some biphenyl structures and 3,4,5-trimethoxy benzaldehyde. These aldehydic compounds could be useful to the industry of aromas and perfumes.

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