Journal of Photochemistry and Photobiology A: Chemistry 155 (2003) 231–241

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Destruction of the organic matter present in effluent from a cellulose and paper industry using photocatalysis

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Received 17 October 2002; accepted 28 October 2002

Abstract

The use of photocatalysis to perform the degradation of the organic matter present in the effluent from a paper and cellulose mill was studied. The best conditions for the photocatalytical process at a laboratory scale were determined using real effluent and an aqueous solution of a pre-degraded lignosulphonate as model, for large-scale studies. The results show that the reaction is little influenced by temperature, the apparent activation energy being between 7.9 and 10.5 kJ/mol, typical of phenol degradation mediated by TiO_2. On the other hand, pH, the use of some additives, and the morphology of the photocatalyst exert a considerable influence on the results. P25 proved to be a better photocatalyst than anatase, giving a 60% higher degradation rate. The addition of hydrogen peroxide in the reactions mediated by P25 resulted in an increase of 173.5% in the efficiency of the photocatalytical process. When compared to the reaction induced by anatase, the increase in efficiency was 354%. The association of TiO_2 and a photosensitizer (zinc phthalocyanine) gave a small increase ($<6\%$) in the reaction efficiency, under laboratory conditions. This behaviour is expected considering that using a medium-pressure mercury lamp is only possible to excite the Soret band of the photosensitizer (around 360 nm), due to the insignificant emission of these lamps in the absorption region characteristic of the Q-band (around 660 nm). On the other hand, the addition of $HPO_4{}^{2-}$ did not result in a significative increase of efficiency to the degradation ($<4\%$). This was attributed to the small amount of cationic and electron-deficient species, compared to the amount of anionic or electron-rich species, between the organic matter to be degraded in the effluent, since the best pH for the degradation are lower than pH_{zpc}. Although the reaction mechanism follows the Langmuir–Hinshelwood model, the degradation rate is at least 100 times faster than the adsorption of the organic matter on the TiO_2, showing that the reactions induced by the active species generated on the surface of the photocatalyst and desorbed to the solid–liquid interface must exert an important rule on the degradation rate. Under the best laboratory conditions, more than 80% of the organic matter is mineralised after 60 min of reaction. The best conditions were tested under solar conditions using a compound parabolic collector (CPC) setup and large volumes of effluent, giving excellent results. The experiments were done using small amounts of TiO_2 (50 mg/l of effluent).

Keywords: Degradation; Lignin fragments; Lignosulphonate; Effluent; Photocatalysis; TiO_2

1. Introduction

Water detoxification is one of the most challenging global problems, principally when the problem is to provide potable water for the population in a non-biodegradable pollutant-rich environment.

A very powerful process, which has been proposed to promote water decontamination, is photocatalysis [1]. The photocatalytic process based on TiO_2 is activated by photons with wavelengths below 390 nm [1,2]. The use of photocatalysis in combination with solar radiation has been shown to be a viable alternative to decontaminate water [3,4]. The viable wavelength range from solar irradiation corresponds to 3–8% of the solar light on the earth surface [5].

Although the reaction mechanism involved is extremely complex, depending essentially on the nature of the substrate, the fundamental steps which enable or inviabilise the photocatalytical process, have been elucidated by flash photolysis and other time-resolved techniques [2]. The excitation of the semiconductor is an extremely rapid step, occurring in a time-scale of femto seconds. For this to

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PII: S1010-6030(02)00393-3

occur, it is necessary that the incident photons have energy higher than the bandgap (E_G) of the semiconductor. For TiO_2, $E_G = 3.2$ eV ($\lambda \leq 390$ nm).

$$TiO_2 + h\nu \rightarrow TiO_2(h^+) + TiO_2(e^-)$$

The next steps are sufficiently rapid (between 100 ps and 100 ns) to viabilise or not the photocatalytical process [22], which occurs in the surface of the semiconductor. The viabilisation or not will depend essentially on the morphology of the semiconductor, and structural defects are important to improve the quantum efficiency of the interfacial charge transfer [2,6].

The interfacial charge transfer occurs in a time interval between 100 ns and some milliseconds. From that, the photocatalytical process effectively begins. Oxidations (from $TiO_2(h^+)$) and reductions (from $TiO_2(e^-)$) can occur simultaneously. From this point, the reaction begins to have a high complexity, involving sometimes the interaction between the substrate and the surface of the semiconductor, or more commonly species with higher mobilities like the solvent, oxygen, etc. [2]. Fundamentally, hydroxyl radicals ($HO^\bullet$) [2,7,8] unleash the most important reactions. Water and hydrogen peroxide are good sources for these radicals [2]. As the formation of radicals from hydrogen peroxide is easier than from water, the addition of hydrogen peroxide in a photocatalytic system usually results in positive increment of the degradation [9–12]. Being an electron acceptor, hydrogen peroxide reacts with conduction band electrons to generate hydroxyl radicals, preventing electron/hole recombination [2,12]. Hydroxyl radicals react efficiently with different substrates in water, with rate constants between 10^7 and 10^{10} l/(mol s) [14,15]. It is recognised as the most efficient oxidant found in the environment, with an oxidation potential of 2.80 V [2,16].

The important steps in a photocatalytical process occur at the interface between the semiconductor and the solution due to very short lifetimes of the free radicals, formed on the surface of the semiconductor. As a result, the reactions involving the substrate behave as if it is adsorbed on the catalyst. A very suitable model to describe the degradation of organic substrates mediated by TiO_2 is the Langmuir–Hinshelwood [2,5]. When the substrate concentration is sufficiently small, it reduces to an order-one rate problem [5].

In this paper, the conditions to perform photocatalysis efficiently to promote the degradation of the organic matter present in the effluent from a paper and cellulose mill is studied.

2. Experimental

2.1. Photolysis system

The laboratory setup consisted of a cylindrical borosilicate glass jacket with a path length of 1.0 cm and a 400 W high-pressure mercury lamp coaxial with it. The average dose of UVA radiation measured for the lamp was 1100 W/m^2. The irradiance measurements were done using a Solar Light PMA2100 photometer/radiometer, equipped with an UVA detector. The suspension containing the photocatalyst and the material to be degraded was pumped into the jacket, being circulated in front of the lamp, with a constant rate of 1350 ml/min. A cooler between the reservoir and the pump was used to control the temperature of the reactional medium during each experiment.

2.2. CPC reactor

A 3.09 m^2 of irradiated surface compound parabolic collector (CPC) reactor was used in the experiments using solar irradiation. The system consisted of 24 borosilicate glass tubes (external diameter 32 mm, wall thickness 1.4 mm, length 1500 mm), divided in three modules, mounted in parallel on double parabolically shaped aluminium reflector surfaces. The concentration ratio is 1.0, the reflectivity of the reflector surface within the bandgap of TiO_2 (300–390 nm) is 89.5%. The tubes are involved with highly reflective sheets in geometry that reflect the irradiation to all the surface. The flow rate was 20 l/min. The measurements were done at the DLR installations, Köln.

2.3. Quantitative analysis

Chemical oxygen demand (COD) was measured using a LASA 100 photometer and a Dr. Lange COD tests cuvettes. The total organic carbon (TOC) analyses were carried out on an Elementar HighTOC II Analyser.

Spectrophotometric measurements were done using a Hach DR4000-U spectrophotometer. Chloride ions were measured potentiometrically, and were taken as an evidence of the presence of organochlorine compounds in the effluent, considering that the degradation of organochlorine compounds must introduce chloride ions in the solution.

2.4. Parameters optimised in the degradation

The studies began by the search of the best conditions to promote the degradation of the organic matter present in the effluent. The following parameters were evaluated: pH, temperature, TiO_2 (anatase 99% (Acros) and P25 (Degussa)), addition of $HPO_4{}^{2-}$ and H_2O_2 (30%, VETEC). The degradation was followed by the changes measured in the chemical oxygen demand, total organic carbon and in the absorbance at 276 nm, characteristic of lignin fragments [21].

2.5. Preparation of the pre-degraded lignosulphonic acid

A sodium salt of a lignosulphonic acid (Aldrich) was modified to be used as model for large-scale experiments. The modifications were introduced under oxidative conditions, in two steps, as described below.

Eight grams of lignosulphonate were diluted in 100 ml of 0.1N NaOH solution. This solution was then pre-heated (40–50 °C). After that, 4 ml of hydrogen peroxide 30% was added, under stirring. The reaction mixture was then heated up to 100 °C and this temperature was maintained for 1 h. After this, 100 ml of an aqueous solution of sodium hypochloride (ca. 5%) was added to the mixture, under heating and stirring. Then, 4 ml of hydrogen peroxide 30% was added in small portions. When the addition was finished, the reaction mixture was maintained under stirring for 1 h. The mixture was acidified, under stirring, with concentrated sulphuric acid (until pH 2 or 3).

Infrared spectra of the lignosulphonate before and after treatment of the photocatalyst and of the solids present in the effluent were done mixing with KBr small amounts of the previously dried substrates. The measurements were performed using a Perkin-Elmer Spectrum 1000 FT Infrared Spectrometer, with a resolution of 16 cm^{-1}.

2.6. Apparent activation energy and pre-exponential factor of the process

The apparent activation energy and pre-exponential factor of the photocatalytical process were estimated considering that the data follow the Arrhenius equation. As the concentration of reactive species generated by the photocatalyst must quickly reach a stationary-state regimen after the beginning of the photocatalytical process, the reaction kinetics were treated as being of pseudo-first order.

2.7. Adsorption kinetics

For the evaluation of the adsorption kinetics of organic material by the photocatalyst, a mixture containing TiO_2 and the solution containing the organic matter was maintained under stirring in the dark at 313 K. At regular time intervals aliquots of the material were collected. After the remotion of the catalyst, the absorbance of the solution at 276 nm was measured. The adsorption kinetics was treated considering that the amount of organic matter is sufficiently low to follow a pseudo-first-order rate law.

2.8. Preparation of the composite TiO_2/ZnPc 10% (w/w)

Zinc phthalocyanine (Sigma) was dissolved in a volume of dimethylformamide under heating and stirring. After this, an amount of TiO_2 sufficient to prepare the photocatalyst with 10% in weight of zinc phthalocyanine was added. The solvent was then evaporated and the photocatalyst was dried at 120 °C.

3. Results and discussion

3.1. General considerations

The problem broached in this study is related to the degradation of the organic matter present in the effluent from a paper and cellulose mill. This effluent is the combination of the effluents from cellulosic pulping (Kraft pulping, using anthraquinone as additive), bleaching and paper production. The expected principal constituents are lignin fragments and inorganic salts, such as sulphates and chlorides. The bleaching process used by the industry is based on an ECF process, and involves the remotion of residual lignin with oxygen, followed by stages using ozone, chlorine dioxide, alkaline extraction and hydrogen peroxide. Actually, this effluent is treated by a combination of decantation and biological treatment to reduce its COD to an acceptable level. In this industrial plant, a considerable volume of effluent is produced (around 2600 m^3/h). To treat each hour of produced effluent, the industry consumes ca. 16 h. The biological treatment is responsible by 50% of this time, and a COD reduction of 98% in the effluent is usually achieved.

The effluent used in this work was collected before it to feed the biological reactor (pH between 6.5 and 7.5). Its COD was between 400 and 500 mg/l, with solids content around 1500 mg/l. It presents a characteristic smell of sulphide due to mercaptans present in the material, possessing a pale yellow colour, with a small amount of particles in suspension.

3.2. Organochlorine compounds in the effluent

The amount of chloride ion during the photocatalytical treatment showed an almost linear growth followed by a stabilisation after 40 min, which was attributed to the mineralisation of the organochlorine compounds present in the effluent. These compounds were produced probably during the bleaching steps involving chlorine dioxide. This can be expected considering that the use of chlorine dioxide reduces significatively the amount of organochlorine derivatives between the final products, but is not capable to eliminate them completely (Fig. 1) [17].

An approximate estimate of the Cl^- formed by the degradation of organochlorine compounds gave a value around 29 ppm.

It is known that chloride ions are usual additives to accelerate some photocatalytical reaction [2]. However, in this case, the previous precipitation of the chloride from the salts present in the effluent, before the photocatalytical treatment, showed that this photocatalytical treatment is not favoured by chloride ions in solution.

3.3. Other considerations

Our previous experiments showed that 50 mg of TiO_2 per litre of the effluent presented as good results as higher

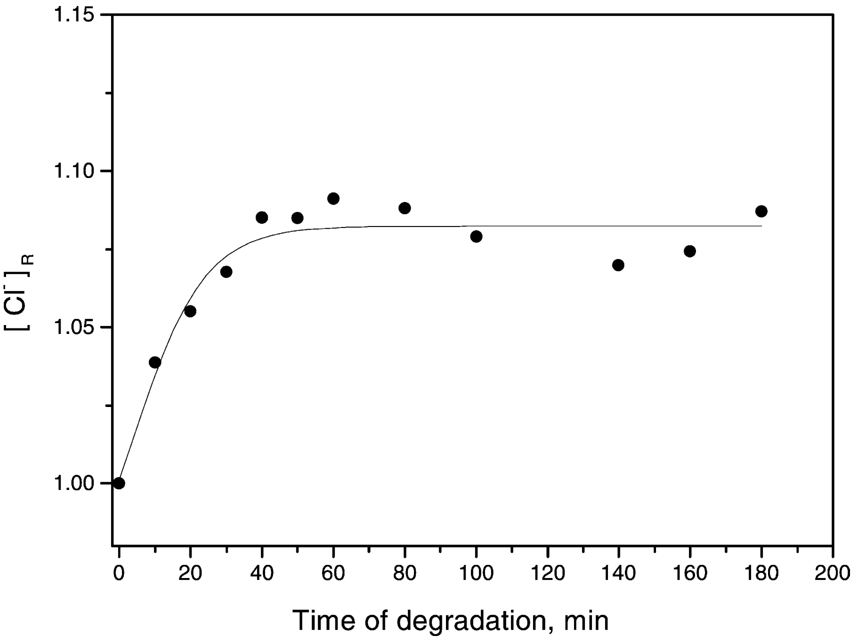

Fig. 1. Relative increase in the chloride ion concentration, monitored during the photocatalytical degradation of the organic matter present in the effluent.

amounts in the laboratory setup. This result must be related to the exceptionally high UVA irradiance of the lamp, at least 17 times the maximum irradiance measured in a summer sunny day in Uberlândia, Brazil (64–66 W/m^2). Considering the cylindrical geometry of the reactor, an invariant irradiance of the lamp in all directions, and that the irradiated area is 134.30 cm^2, a simple mathematical exercise gives us an estimate of the incident amount of photons per second. Taking into account the irradiance of the lamp, and 390 nm as the maximum wavelength to reach the photocatalytical effect, the amount of photons per second per irradiated area is 2.91×10^{19} m^{-2} s^{-1}, or 4.83×10^{-5} einstein/(m^2 s). Considering that each discrete particle of the photocatalyst is composed by 4.16×10^5 TiO_2 molecules [2], and that the concentration of TiO_2 in suspension is 50 mg/l, the molar concentration of particles in solution is approximately 1.5 nM. With this value and the flow in the reactional system, we can estimate the mean time lapse for each TiO_2 molecule excited by a second photon as being around 3 ms. This must compensate the usually low quantum efficiency of the photocatalytic processes [2]. This excitation frequency also explains, at least partly, why the concentration of TiO_2 proved to be unimportant for these experiments.

3.4. Degradation tests using a pre-degraded lignosulphonate as model

To viabilise large-scale tests, the search of a suitable model which reproduce the behaviour (to be soluble in a large range of pH, including acidic pH, and to present the degradability observed for the organic matter present in the effluent) was done. A previously degraded sample of lignosulphonate was found to approach to the required behaviour.

The pre-degradation was needed because, though the lignosulphonate has been found to be soluble in a large range of pH, its degradation pattern, as shown in Fig. 2, was not comparable to that observed for the organic matter present in the effluent, probably due to its high molecular weight (52,000 Da).

The best pre-degradation conditions involved oxidative conditions, which approach the expected to occur during the cellulose pulp bleaching. In this process, the remaining lignin becomes more fragmented and polar.

The analysis of the FTIR spectra of the organic fragments present in the effluent shows the presence of a band at 1737 cm^{-1} characteristic of carboxylic groups, possibly formed during the bleaching process. The spectra also show similarities observed for lignins that contain guayacyl groups (Fig. 3) [21].

On the other hand, the FTIR spectra of the lignosulphonate before and after the pre-treatment apparently do not show similarities with the observed for the organic matter present in the effluent. However, the introduced changes could approach the degradation to the required behaviour. Probably, the changes must be mainly related to the fragmentation of the macromolecule that occurred during the pre-treatment.

Fig. 4 presents a useful calibration curve that makes possible the preparation of solutions at pH 3 with a lignosulphonate content corresponding to a COD previously designed. This calibration curve has been used to prepare the solutions containing the model for large-scale degradation studies, simulating the initial conditions found for the effluent from the cellulose and paper industry.

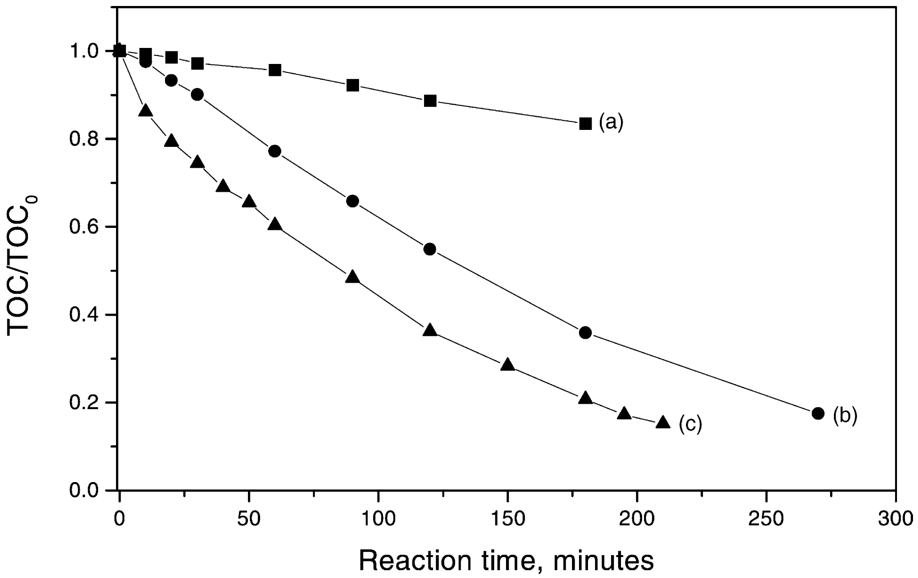

Fig. 2. Photocatalytical degradation of a lignosulphonate solution at pH 3: (a) lignosulphonate; (b) lignosulphonate pre-degraded; (c) effluent. Conditions: pH 3; 0.16 g/l of lignosulphonate + 50 mg/l TiO_2 (P25) + 1 ml/l HOOH 30%.

3.5. pH and [HOOH]

Fig. 5 shows the dependence of k^I on pH. As can be seen, the observed degradation is strongly dependent on pH, occurring efficiently at pH below 4.0. At this pH, the catalyst is positively charged, considering that the pH_{zpc} for anatase is around 4 [23], and for Degussa P25 TiO_2, $pH_{zpc} = 6.25$ [2]. It is very probable that the predominating reaction centres in the compounds to be degraded must be anionic groups, which can act as electron donors for the semiconductor oxide. This agrees with the expected, considering the degradation induced on these fragments during the bleaching of the cellulose pulps, where oxidative reactions were used to promote the transfer of the residual lignin present in the cellulose pulp to the effluent.

Based on the observed trend, the posterior experiments were done at pH around 3. Another important data from these experiments is the effect of the addition of hydrogen peroxide. As can be seen in Table 1, the addition of hydrogen peroxide has a positive effect on the degradation.

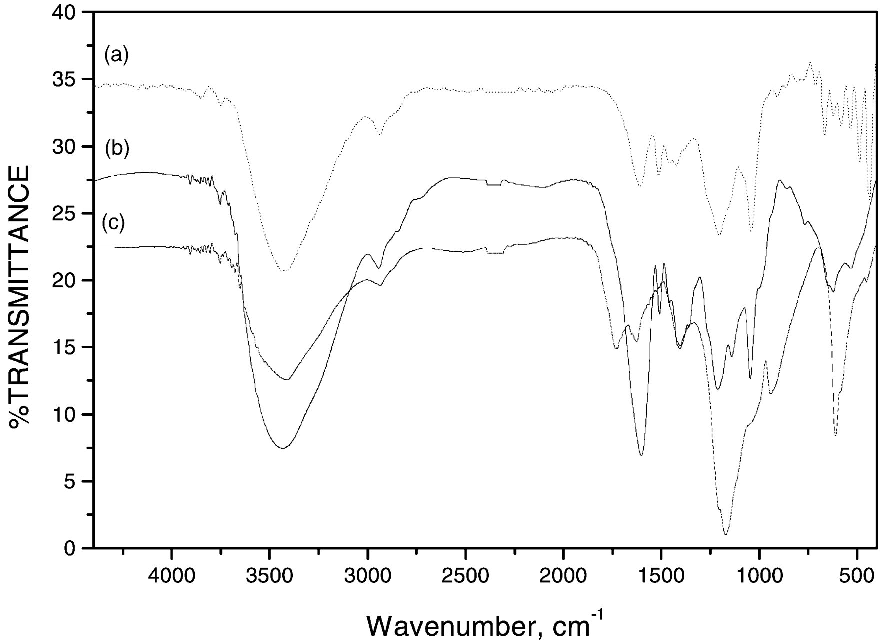

Fig. 3. Infrared spectra: (a) lignosulphonate; (b) pre-degraded lignosulphonate; (c) organic matter present in the effluent.

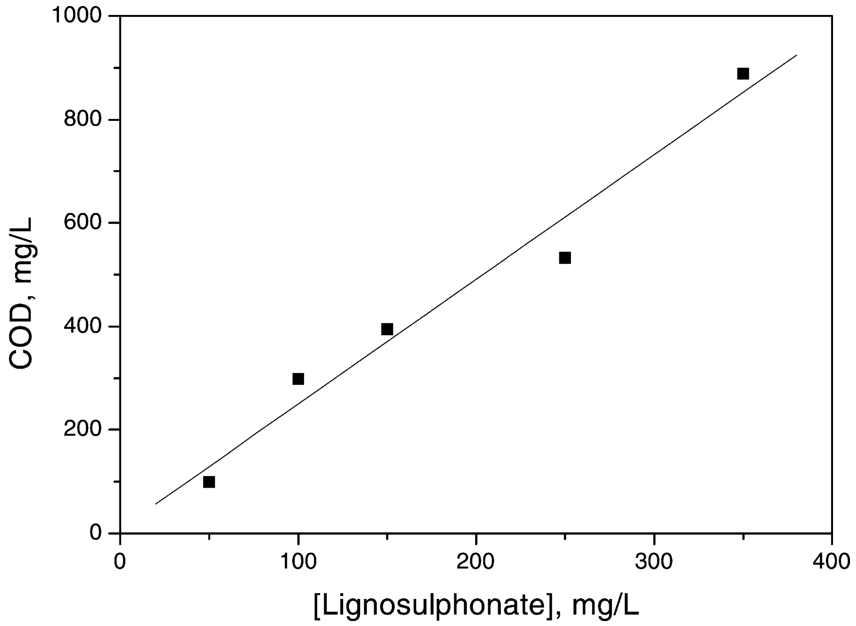

Fig. 4. Calibration curve at pH 3.0 for preparation of solutions containing pre-degraded lignosulphonate for tests (COD = 8.726+2.411 (lignosulphonate)).

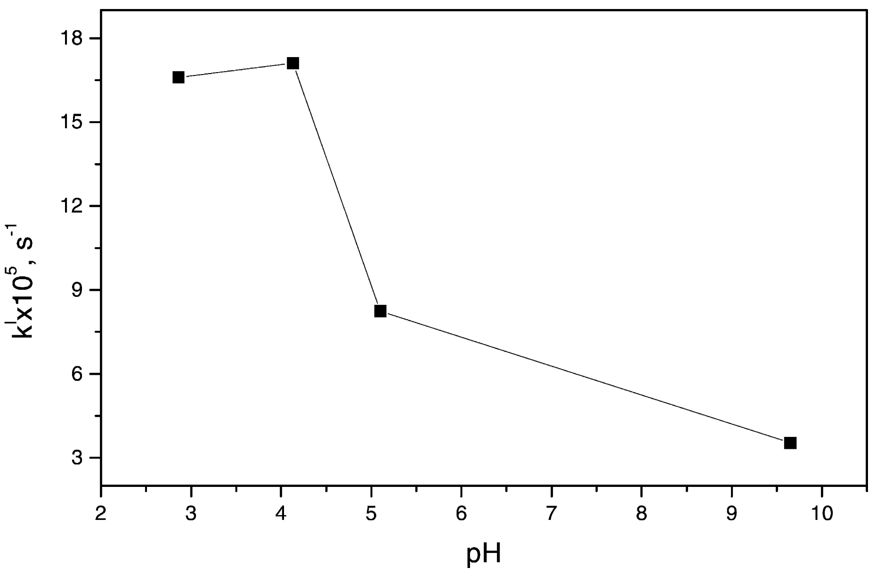

Fig. 5. Effluent degraded under different pH, using 50 mg of anatase/l, at 313 K.

The addition of HOOH implies an increase between 20 and 30% in the reaction rate. Although the improvement reached for the degradation mediated by P25 was higher than this (Table 3), showing that the use of $TiO_2(e^-)$ by the added hydrogen peroxide molecules to generate hydroxyl radicals is more effective for this photocatalyst. This must be related to the higher specific area ($50\,m^2/g$) and porosity estimated for TiO_2 P25 [28]. Otherwise, the specific area estimated for the anatase (Acros) was around $8\,m^2/g$ [27].

Table 1
Degradation rates at pH 2.96, for different amounts of HOOH

HOOH 30% (ml/l)	$k \times 10^4$ (s^{-1})	k/k_0
0.0	1.66	1.00
0.5	1.98	1.19
1.0	2.16	1.30
2.0	1.97	1.19

3.6. *Temperature: apparent activation energy*

Since the photonic activation occurs at considerably high speeds, it is expected that the photocatalytic system is not sensible to the temperature, and the true activation energy

Table 2
Apparent activation energies for the degradation of the organic matter present in the effluent and of the lignosulphonate and pseudo-first-order kinetic constants for the adsorption of the organic matter

	E_a (kJ/mol)	A (s^{-1})	k_{ads} (s^{-1})
Effluent/P25	7.91	2.63×10^{-3}	2.29×10^{-6}
Effluent/anatase	10.44, 10.50	6.38×10^{-3}, 6.77×10^{-3}	–
Lignosulphonate/ P25	8.65	1.82×10^{-3}	3.63×10^{-6}
Lignosulphonate/ anatase	–	–	1.61×10^{-6}

must be then equal to zero. Although considering that the reactions under study occur preferentially in the liquid/solid interface, a non-zero value must be expected as an apparent activation energy. With the increase of temperature, the exothermic adsorption of the reactants becomes disfavoured due to the increase in the entropy of the solvent, which can reduce the value of the apparent activation energy. The apparent activation energy found is between 7.9 and 10.5 kJ/mol for both photocatalysts, as can be seen in Table 2. These values agree with typical values found for phenol degradation mediated by TiO_2 [24].

Fig. 6 shows a typical graph obtained in the estimation of the apparent activation energy. Unfortunately, values for comparison for lignin photocatalytical degradation mediated by P25 could not be found. Villaseñor and Mansilla [25] have reported an apparent activation energy of 43.1 kJ/mol for the photocatalytical mineralisation of lignins present in a Kraft black liquor, mediated by ZnO. However, a direct comparison between these two results is difficult, considering the differences inherent to these two semiconductors. On the other hand, the value found for anatase and P25 can be taken as an indicative that the major species present in the effluent are phenol-based structures. This is confirmed by inspection of the infrared (Fig. 2) and ultraviolet/visible spectra (Fig. 7) of these compounds.

A small dependence of the spectra with pH occurs near 275 nm, due to the protonation/deprotonation of the phenolic and carboxylic groups [13,21].

The pre-exponential factor usually assumes large values for efficient processes [26]. This parameter is usually related to changes in entropy on going from the reactant to the transition state. The values found are considerably small (Table 2). However, it is difficult to conclude anything at this point since this parameter was approximately estimated for the global process.

3.7. Adsorption of organic matter on the photocatalyst

It is well accepted that the mineralisation of the organic matter induced by photocatalysis follows a Langmuir–Hinshelwood kinetics [2,19]. According to the Langmuir–Hinshelwood model, the adsorption rate of a particular specie is proportional to the fraction of surface covered by the substrate (ϑ), and its degradation rate can be written as

$$\frac{d[S]}{dt} = k_1 \frac{\sigma_0 K_S[S]\prod_i K_i[S_i]}{1 + K_S[S] + \sum_i K_i[S_i]}$$

where [S] is the concentration of a particular substrate, k_1 is its degradation rate, σ_0 the number of disponible sites on the surface, $\Pi K_i[S_i]$ and $\Sigma K_i[S_i]$ are amounts related to the species that compete with the degradable substrate.

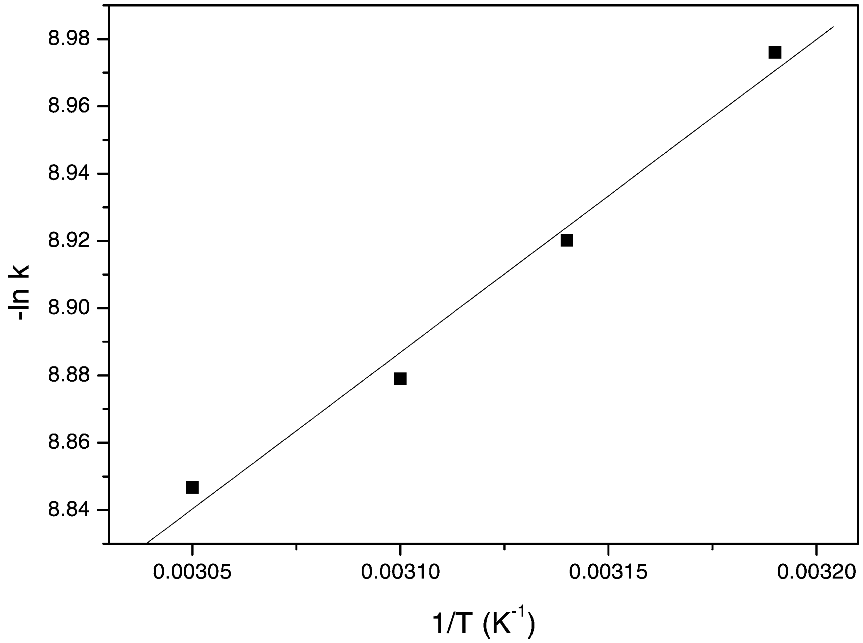

Fig. 6. Typical graph of $-\ln k \times 1/T$ for the degradation of the organic matter present in the effluent, using P25. Relative error = 8.97%.

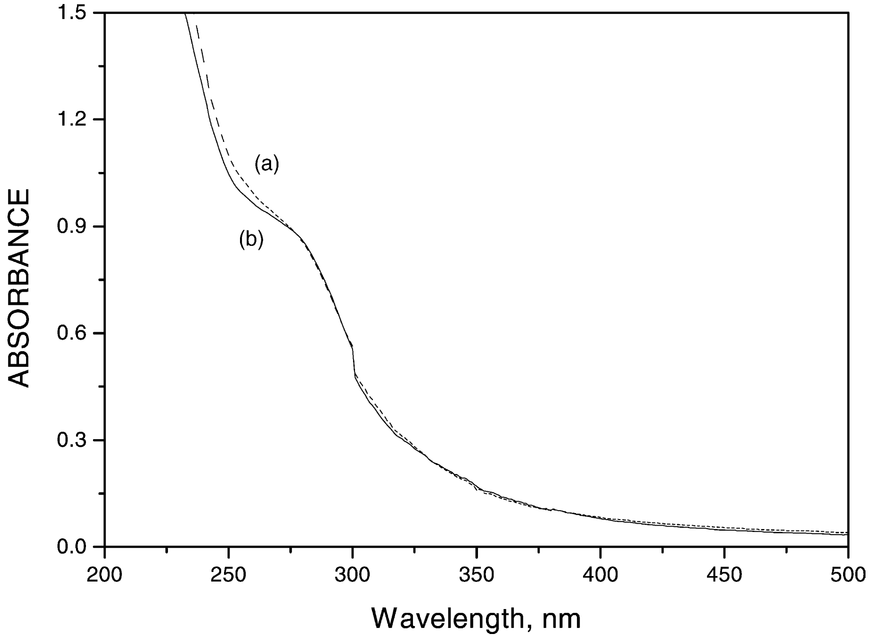

Fig. 7. UV-Vis spectra of the organic matter present in the effluent: (a) pH 3.20; (b) pH 9.41. These spectra are typical of lignins (Fengel).

The amount

$$K_i = \left(\frac{k_a}{k_d}\right)_i = \left(\frac{[S_{ads}]}{[S]}\right)_i$$

is the adsorption/desorption equilibrium constant of a particular specie present in solution. Assuming that the concentration of other species excluding the organic matter, must remain unaltered in our experiments, the rate law can be reduced to

$$-\frac{d[S]}{dt} = k_{obs}[S]$$

with

$$k_{obs} = \frac{k_1 \sigma_0 K_S \prod_i K_i [S_i]}{1 + \sum_i K_i [S_i]}$$

and the adsorption kinetics of the organic matter present in the effluent can be treated as the first-order process.

Since the adsorption of the organic matter occurs at a very low rate, being at least 100 times lower than the values estimated for its degradation, it is plausible to consider that the reaction must occur preponderantly with the substrate and the generated (desorbed) radicals at the interface between the surface of the photocatalyst and the solution. On the other hand, the adsorption rates of other species like water and hydrogen peroxide must be higher, considering their mobilities and concentrations in the reactional system. As the radical concentrations must reach rapidly a stationary state, the degradation of the organic matter can also be treated as a pseudo-first-order process. Fig. 8 shows a typical adsorption kinetics for this kind of organic matter.

The pseudo-first-order kinetic constants measured for the adsorption of the organic matter by P25 and anatase can be seen in Table 2. Due to its higher specific surface, the relative adsorption of the organic matter on P25 is higher than the observed for anatase.

3.8. *Anatase versus P25: addition of HPO_4^{2-} and tests involving zinc phthalocyanine adsorbed on TiO_2*

Table 3 and Fig. 9 show the degradation rates, at pH 3, for the effluent (initial COD = 400 ± 50 mg/l), using a constant amount (50 mg/l) of anatase or P25. The pseudo-first-order degradation rates were estimated for the first 60 min of reaction.

Previous tests using TiO_2 (anatase) 99% as photocatalyst gave good results, but P25 proved to be more efficient as photocatalyst, giving a 60% higher degradation rate. This behaviour must be in a great part related to its higher specific surface. This agrees with the analysis of the infrared spectrum of P25, which shows a relative content of OH higher than the verified for anatase (Fig. 10).

Table 3
Degradation rates for the effluent under different conditions

Reaction conditions[a]	k (s^{-1})	k/k_a
(a) Anatase 99%	9.08×10^{-5}	1.000
(b) P25	1.45×10^{-4}	1.597
(c) P25 + HPO_4^{2-}	1.51×10^{-4}	1.663
(d) P25 + HPO_4^{2-} + HOOH	4.12×10^{-4}	4.537
(e) P25/ZnPc 10% (w/w) + HOOH + HPO_4^{2-}	4.37×10^{-4}	4.813

k_a:k (anatase).

[a] 50 mg TiO_2 per litre; pH 3; initial COD 400 ± 50 mg/l; 1 ml HOOH per litre; 25 mg HPO_4^{2-}/l; 318 K.

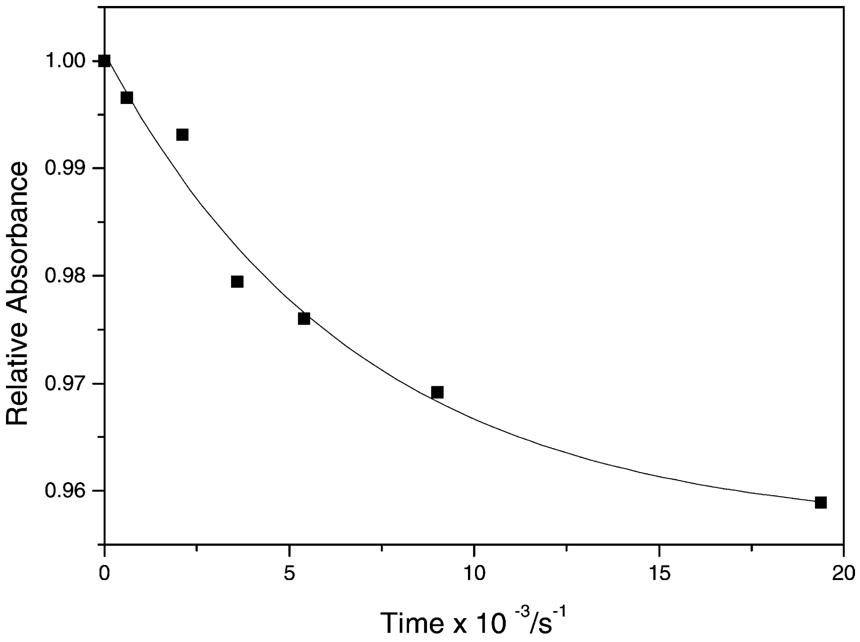

Fig. 8. Typical adsorption profile for the organic matter dispersed in water by TiO_2: adsorption of a model (pre-degraded lignosulphonate) in P25 (50 mg/l) at pH 3 and 313 K.

This data is related to the number of active sites in the catalyst, able to produce hydroxyl radicals [18] from electron-donor substrates, like water, aromatics, oxygen, etc. [18,20] and explains, at least in part, the relative efficiency observed for P25. Other parameters related to its morphology, like the presence of favourable structural defects also must have great influence on the results.

The results indicate that modifications on the surface of TiO_2 (P25) introduced by HPO_4^{2-} only resulted in a small enhancement (<4%) of the photocatalytic degradation, when compared with the previous result. This leaves us to consider that some residual components in this effluent have cationic character. Vohra and Tanaka [23] have proposed that the addition of HPO_4^{2-} must favour the degradation of cationic species. At the pH of the reaction, the TiO_2 surface must be preponderantly positive, which will favour the degradation of anionic or electron-rich species, the majority fragments, considering the good degradability of the organic matter at $pH < pH_{zpc}$ [2].

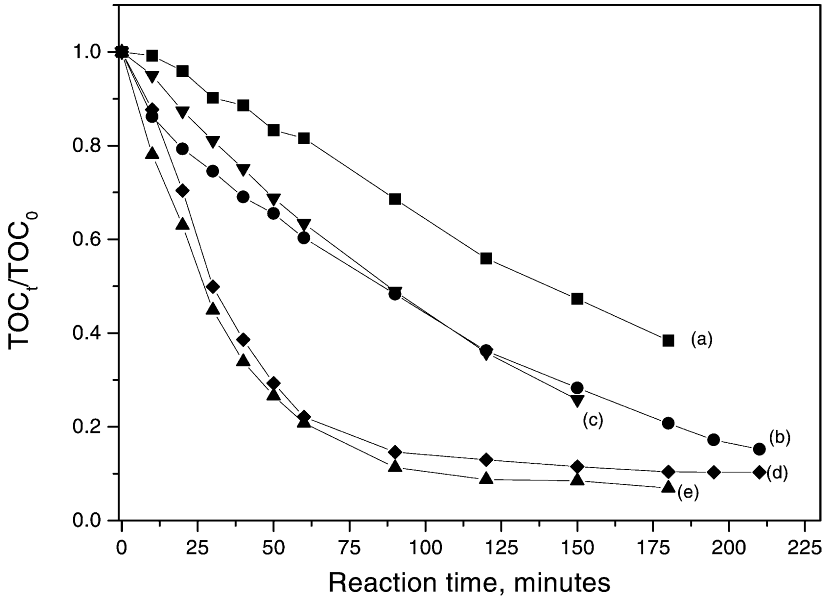

Fig. 9. Degradation of the effluent using anatase 99% or P25 (Degussa): (a) anatase 99%; (b) P25; (c) P25 + HPO_4^{2-}; (d) P25 + HOOH + HPO_4^{2-}; (e) P25/ZnPc 10% (w/w) + HOOH + HPO_4^{2-}. Conditions: 50 mg TiO_2/l; initial COD 400 ± 50 mg/l; 1 ml HOOH/l; 25 mg HPO_4^{2-} per litre; 318 K.

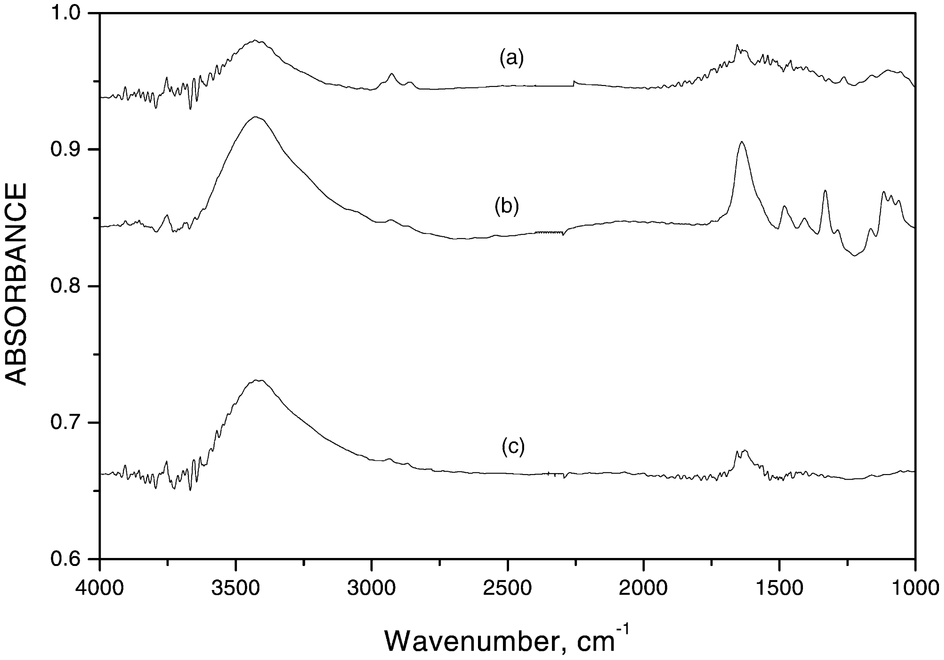

Fig. 10. Infrared spectra of (a) anatase; (b) P25/ZnPc; (c) P25.

The inclusion of hydrogen peroxide (1 ml/l of effluent) resulted in improvement of the degradation rate of around 173.5%, when compared this result with the previous, or of 354%, when compared to the result obtained with anatase, indicating, as expected, that hydrogen peroxide is an important font of radicals for this reaction [2].

On the other hand, the use of the composite P25/ZnPc 10% (w/w) as photocatalyst gave a small improvement (<6%) to the degradation rate. This apparently could be seen as a bad result. However, it can be explained considering that these reactions were performed using an HPL-N mercury lamp, which does not present significative emission in the region of the Q-band of the zinc phthalocyanine, around 660 nm. The action of the zinc phthalocyanine, possibly injecting electrons to the conduction band of the catalyst, is due to the excitation of the Soret band, around 360 nm.

The electron transfer from the photosensitizer to the semiconductor seems to be promising to the enhancement of the photocatalysis [29–40], since the font of photons give a good irradiance in regions of the electromagnetic spectrum incapable to promote directly electrons from the valence to the conduction band of the semiconductor, but easily absorbed

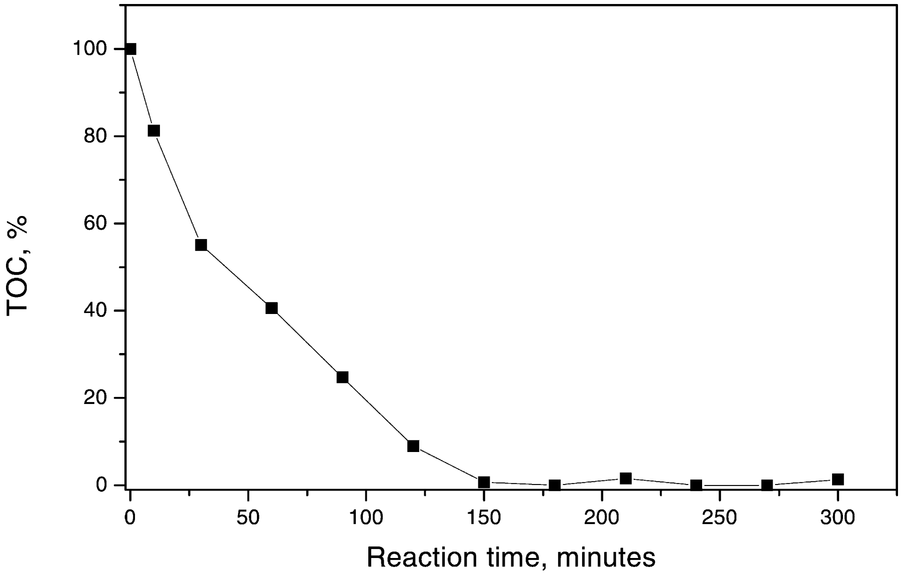

Fig. 11. Photocatalytic degradation of the lignosulphonate using solar radiation.

by the dye or pigment associated with the catalyst. It is probable that these composites must present incomparable efficiencies when sun is the font of radiation.

3.9. Initial CPC test

Sixty litres of a lignosulphonate solution containing 8 g of the pre-degraded lignosulphonate, with an initial TOC of 70 mg/l, was submitted to degradation using a 3.0 m^2 CPC reactor. The initial pH of the solution was around 3 and the organic matter was degraded by photocatalysis using solar radiation. A volume of 150 ml of HOOH and 3 g of TiO_2 (P25 Degussa) were added to the reaction system. The result is shown in Fig. 11.

An efficient degradation of the organic matter was achieved, as can be seen from the analysis of the changes in the content of TOC during the reaction. The TOC is practically zeroed after a reaction time of 150 min. This is an indication that all organic matter present in the effluent was mineralised. The observed trend is quite similar to that observed in the experiments done in the laboratory, employing lower volumes of the solution containing the lignosulphonate. Experiments are now being done, using the CPC technology and different formulations of the photocatalyst, and aiming to establish the best conditions to perform the degradation under solar conditions.

Acknowledgements

CNPq, DLR, IB/BMB + F and FAPEMIG are acknowledged for research grants, and Votorantim Celulose e Papel (VCP) for kindly furnishing the effluent under study.

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