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***DEGRADATION OF ORGANIC COMPOUNDS IN PAPER AND  
TEXTILE INDUSTRIAL WASTEWATERS BY ADVANCED  
OXIDATION PROCESSES***

**Memòria presentada per optar al grau de Doctora en Enginyeria Industrial**

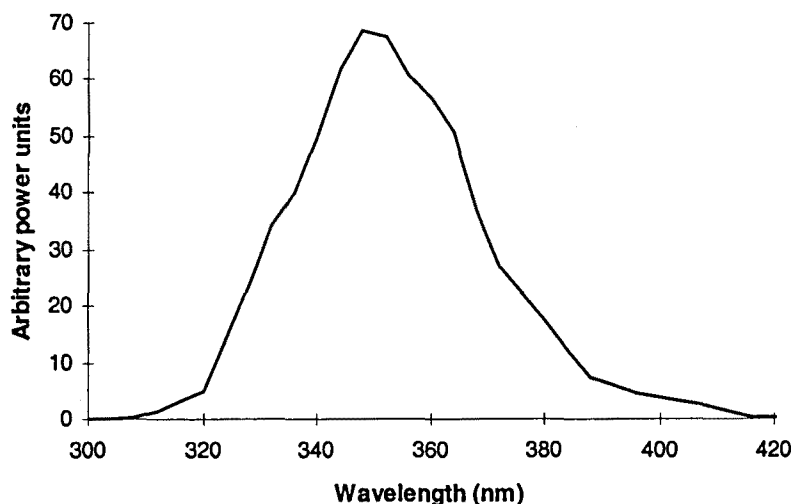
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**Terrassa 2001**

## ANNEX 1: Light Irradiation

### UVA light

The black-light fluorescent lamp spectrum provided by the Phillips supplier is shown in Figure 1 in arbitrary power units. The lamp power is 6 W. The spectrum shows that the majority of irradiation is concentrated in the near UV and visible zone. The site of maximum intensity corresponds to 348 nm wavelength. Consequently, this source of light is especially well suited for photocatalytic treatment. Besides, the irradiation is appropriate for mixtures of Fe(III) + H<sub>2</sub>O<sub>2</sub> (Fenton-like reactions) and both extremes of the of the spectrum would be useful in ozone processes ( $\lambda < 310$  nm) or for photo-Fenton reactions ( $\lambda$  close to 400nm).



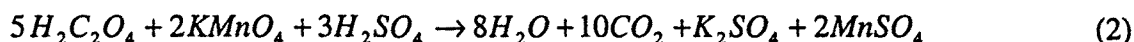
**Figure 1.** *Emission spectrum of the Phillips black light lamp.*

The information provided by the Phillips supplier is not sufficient for our purposes because we need to know the intensity, Einsteins·s<sup>-1</sup>, and the power which arrive at the studied samples for every wavelength. In order to obtain those values, an uranyl actinometry was performed.

Mixing solutions of uranyl sulfate and oxalic acids produced uranyl oxalate complexes: UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. These complexes absorb light in the ultraviolet and sensitize the decomposition of the oxalate ions according to the overall reaction:



The number of moles of oxalate transformed during the irradiation period is determined by titrating the oxalate actinometric solution, before and after irradiation, with potassium permanganate:



From the titration value, it is possible to calculate the number of photons absorbed by the actinometry solution.

The quantum yield of disappearance of the oxalate ions is approximately 0.55 between 278 nm and 436 nm. Figure 2 represents the quantum yield of disappearance of uranyl oxalate for each wavelength.

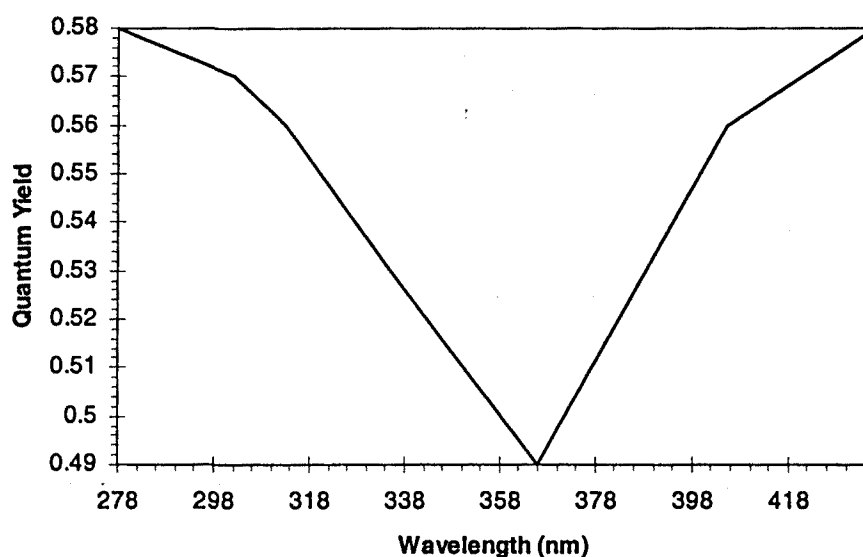


Figure 2. Quantum yield of disappearance of uranyl oxalate.

The surface of our batch reactor was  $23.75 \text{ cm}^2$  and the distance from the light source to the liquid was 5 cm. Our results with the actinometry performed under the described conditions told us that  $1.5255 \cdot E15 \text{ photons} \cdot \text{s}^{-1}$  reach the reactor. Considering the quantum yield, it is possible to calculate that  $8.328 \cdot E14 \text{ photons} \cdot \text{s}^{-1}$  or  $1.383 \cdot E-9 \text{ Einstein} \cdot \text{s}^{-1}$  are absorbed in the actinometric solution.

An iterative calculation method based on a scale change is applied in order to know the real power for each wavelength. It is important to note that the spectrum of real values should follow the same distribution as the one provided by the supplier in Figure 1.

The maximum power in arbitrary units as shown in Figure 1 is 68.5. A new maximum value based on the new scale is proposed in order to initiate the iterative calculation (the

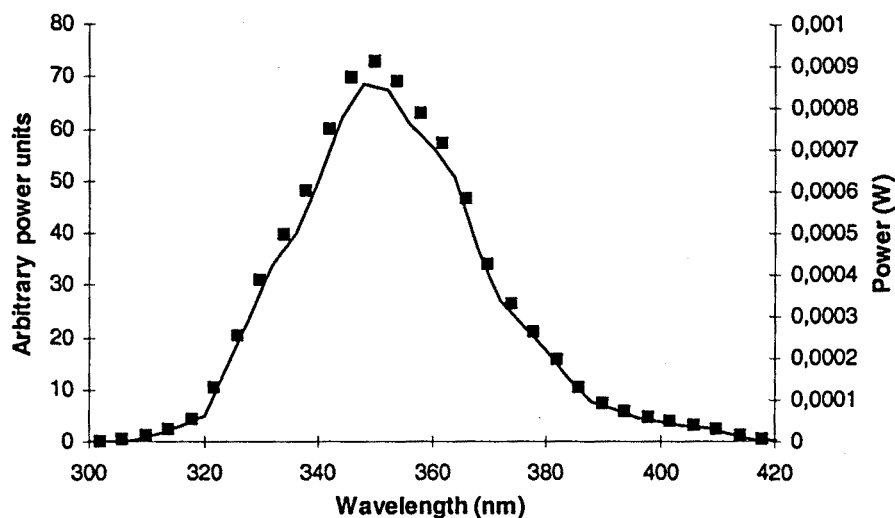
second column of Table 1 displays the scale change.) From the new power values intensity values are obtained, Einstein·s<sup>-1</sup>, (third column of the same table). To finish the calculation, it is necessary to make the correction of the quantum yield. The values of the fourth column of the table are obtained from Figure 2. The last column represent the total number of Einsteins·s<sup>-1</sup> for every absorbed wavelength of the actinometric solution.

The iteration should be repeated until the addition of all the values in the last column coincide with the value obtained from the actinometry, 1.383·E-9 Einstein·s<sup>-1</sup>. For each iteration a new maximum value for the new scale is chosen. This value should be either bigger or lower than the previous one, which was used to determine the obtained result, depending on the final obtained value. The following table it is a summary of the values obtained from the last iteration. The table displays the Einsteins·s<sup>-1</sup> received by the samples at every wavelength.

Table 1. Results obtained from the last iteration in the calculation process.

$\lambda$ (nm)	Power (W)	Einsteins $\cdot$ s $^{-1}$	Quantic Yield	Einsteins $\cdot$ s $^{-1}$
302	0	0	0,57	0
306	3,3324E-07	8,5241E-13	0,566	4,8246E-13
310	1,3329E-06	3,4542E-12	0,563	1,9447E-12
314	2,9991E-06	7,8723E-12	0,559	4,4006E-12
318	5,3318E-06	1,4173E-11	0,553	7,8379E-12
322	1,2663E-05	3,4085E-11	0,547	1,8645E-11
326	2,5326E-05	6,9017E-11	0,542	3,7407E-11
330	3,8655E-05	1,0663E-10	0,537	5,7263E-11
334	4,9319E-05	1,377E-10	0,531	7,3119E-11
338	5,9982E-05	1,6948E-10	0,526	8,9146E-11
342	7,4645E-05	2,134E-10	0,521	1,1118E-10
346	8,6974E-05	2,5156E-10	0,515	1,2955E-10
350	9,064E-05	2,6519E-10	0,511	1,3551E-10
354	8,5641E-05	2,5343E-10	0,505	1,2798E-10
358	7,831E-05	2,3436E-10	0,5	1,1718E-10
362	7,1312E-05	2,158E-10	0,495	1,0682E-10
366	5,7983E-05	1,774E-10	0,49	8,6927E-11
370	4,2321E-05	1,309E-10	0,497	6,5056E-11
374	3,2657E-05	1,021E-10	0,504	5,1458E-11
378	2,6326E-05	8,3185E-11	0,511	4,2508E-11
382	1,9661E-05	6,2783E-11	0,519	3,2584E-11
386	1,2996E-05	4,1935E-11	0,526	2,2058E-11
390	8,9974E-06	2,9333E-11	0,533	1,5634E-11
394	6,9979E-06	2,3049E-11	0,54	1,2446E-11
398	5,665E-06	1,8848E-11	0,547	1,031E-11
402	4,6653E-06	1,5678E-11	0,555	8,7011E-12
406	3,6656E-06	1,2441E-11	0,559	6,9544E-12
410	2,6659E-06	9,1369E-12	0,561	5,1258E-12
414	1,3329E-06	4,613E-12	0,564	2,6018E-12
418	6,6647E-07	2,3288E-12	0,566	1,3181E-12
422	3,3324E-07	1,1755E-12	0,569	6,6889E-13

To ensure that the power spectrum obtained from the calculations follow the same pattern as the spectrum provided by the supplier (Figure 1), both spectrums are superimposed as is shown in Figure 3.



**Figure 3.** Emission spectrum of the 6 W Phillips lamp as provide by the supplier (—). Total irradiation power which reached the reactor using a 4 nm window (■).

The following table summarizes the more relevant characteristics of the studied light source.

**Table 2.** Intensity and power received by the samples studied.

Intensity absorbed by the actinometre (Einsteins·s <sup>-1</sup> )	1.383·10 <sup>-9</sup>
Reactor surface (cm <sup>2</sup> )	23.75
Total power input in the reactor (W)	9.104·10 <sup>-4</sup>
Power per surface (W·cm <sup>-2</sup> )	3.833·10 <sup>-5</sup>

## Xenon lamp

The 250 W Xenon lamp (Applied Photophysics) spectrum provided by the supplier is shown in Figure 4 in arbitrary power units. The spectrum shows that the main irradiation is concentrated in the near UV and the visible zone, with a maximum signal in the 450 nm wavelength. The lamp irradiated in a wider wavelength interval and thereby is more suitable for photochemically enhanced Fenton reactions, photocatalysis, ozonation etc.

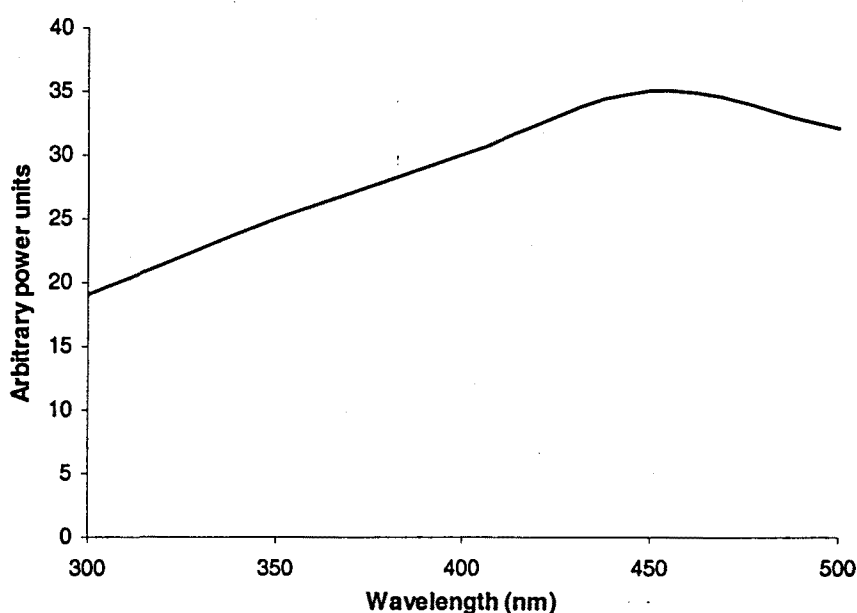


Figure 4. Emission spectrum of the Xenon lamp.

As mentioned for the previous artificial light, the information provided by the supplier it is not specific enough. In order to obtain concrete data, the same method is applied to the 250 W Xenon lamp as it was applied to the black-light fluorescent lamp.

During the actinometric analysis, the same reactor was used and the experimental setup was the same than the one used in the regular experiments. When the reactor is under the Xenon light irradiation,  $8.33 \cdot E16$  photons $\cdot s^{-1}$  arrive at the reactor. Considering the quantum yield, it is possible to determine that  $4.55 \cdot E16$  photons $\cdot s^{-1}$  or  $7.55E-08$  Einstein $\cdot s^{-1}$ , are absorbed by the actinometric solution.

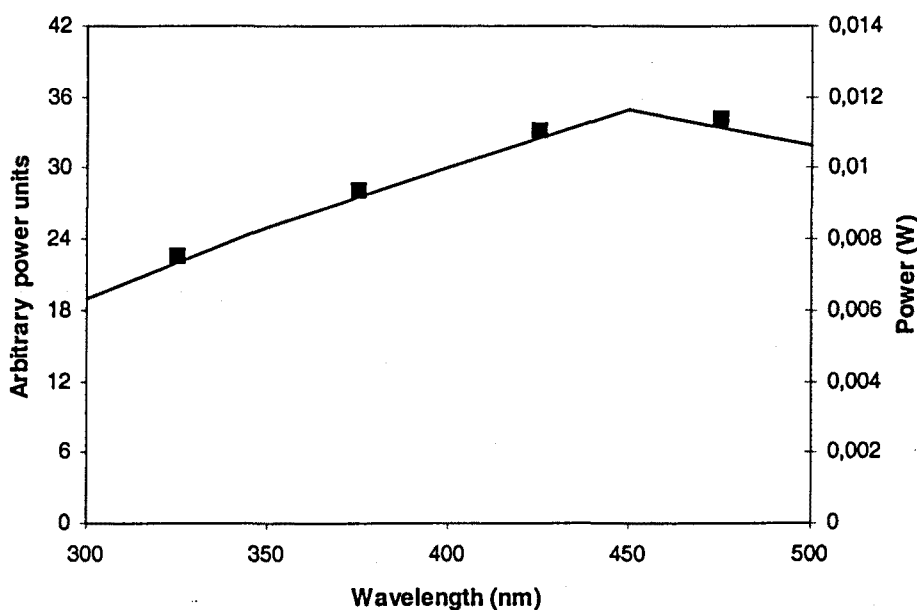
The same iterative process is performed using as a template Figure 4, the quantum yield, and the actinometry data. In this case, as Figure 4 shows, 35 is the maximum power value in arbitrary units. The iterative process is the same as before and continues

until the addition of the last column values equals  $7.55 \cdot 10^{-8}$  Einstein $\cdot$ s $^{-1}$ , the value obtained by actinometry. The following table shows the last iteration values obtained and, more specifically, the intensity and power received by the studied samples for every wavelength.

**Table 3.** Results obtained from the last iteration in the calculation process.

$\lambda$ (nm)	Power (W)	Einsteins $\cdot$ s $^{-1}$	Quantic Yield	Einsteins $\cdot$ s $^{-1}$
325	0,00748	2,0322E-08	0,57	1,1583E-08
375	0,00935	2,931E-08	0,566	1,659E-08
425	0,01105	3,9258E-08	0,563	2,2102E-08
475	0,01139	4,5227E-08	0,559	2,5282E-08

To ensure that the power spectrum obtained from the iteration process follows the same pattern that the one provided by the supplier in Figure 4, both spectra are superimposed as shown in Figure 5.



**Figure 5.** Emission spectrum of the Xenon lamp as the supplier provide (—). Total light irradiation power which reach the reactor in a 50 nm window (■).

The more relevant parameters of the studied light source applied in the experimental setup are collected in Table 4.

**Table 4.** Intensity and power that receive the studied samples in the specific mentioned working conditions.



Intensity absorbed for the actinometre (Einsteins·s <sup>-1</sup> )	7.55·10 <sup>-8</sup>
Reactor surface (cm <sup>2</sup> )	23.75
Total power input in the reactor (W)	3.927·10 <sup>-2</sup>
Power per surface (W·cm <sup>-2</sup> )	1.653·10 <sup>-3</sup>

All these calculations are valid for the specific reactor, experimental setup, actinometry solution, light source, etc. Any change lead to need corrections in the result values.

## ANNEX 2: Bleaching effluents

### Laboratory generated paper pulp effluents

Both bleaching effluents were obtained from the same initial raw pulp, which was sent to two different bleaching processes. The raw material, *Eucalyptus globulus* chips, were classified to ensure a homogeneous thickness during the cooking stage. Cooking process was performed under the following conditions:

**Table 1.** *Characteristic parameters of the cooking process in a laboratory batch reactor.*

<b>Active alkali<sup>a</sup></b> (related to oven dry wood, expressed as % Na <sub>2</sub> O)	17
<b>Sulfidity<sup>b</sup></b> (%)	30
<b>Oven dry wood</b> (kg)	2.2
<b>Liquor-to-wood ratio</b>	4:1
<b>Cooking time</b> (h)	3
<b>Maximum temperature</b> (°C)	170

<sup>a</sup> Na<sub>2</sub>S + NaOH; <sup>b</sup> Sodium sulfur/Active alkali

The white liquor was prepared following the procedures of García Hortal et al. [García Hortal and Colom, 1992].

After the cooking process was completed, the Kappa number was determined to be 20.6 and the viscosity of the pulp was determined to be 650 cm<sup>3</sup>·g<sup>-1</sup>.

Following the cooking process, two different bleaching sequences were performed on the raw pulp to obtain sample effluents with different contamination loads. In each case, elemental chlorine was not present, so procedures related to ECF sequences are applicable.

### First laboratory generated paper pulp effluent

The pulp bleaching process follow an ECF sequence, AOD (acid pretreatment (A) followed by an oxygen delignification (O) and, lastly, a chlorine dioxide bleaching (D)) leading to the complete substitution of chlorine by chlorine dioxide. The studied effluent is collected from the 100 % ClO<sub>2</sub> chlorination stage.

The reason for the acid pretreatment is to eliminate the metallic ions present in the raw pulp. The metallic ions catalyze the formation of free radicals which cause a chain depolymerizing reaction of carbohydrates. The acid pretreatment converts the metallic ions to soluble salts which do not catalyze cellulose degradation in the bleaching stages that follow. Table 2 shows the conditions of the acid pretreatment.

**Table 2.** *Characteristic parameters of the acid pretreatment.*

Acid pretreatment	
Consistence (%)	15
Temperature (°C)	75
Time (min)	25
H <sub>2</sub> SO <sub>4</sub> 2 mol·L <sup>-1</sup>	2 %

After the acid pretreatment, a washing step is performed before the oxygen delignification step. Oxygen will be the first chlorine-free reagent used in the prebleaching of chemical pulps. The oxygen delignification step is very efficient and leads to an important reduction in the Kappa number and also generates effluents that can be reused because of their non-corrosive character. The reduction of residual lignin in the pulp leads to a decreased demand for bleaching agents in later bleaching steps and fewer chlorinated organic compounds formed, when the bleaching steps involve some chlorine compounds used as bleaching agents. Table 3 shows the processing conditions of the oxygen delignification step.

**Table 3.** *Characteristic parameters of the oxygen delignification step.*

<b>Oxygen delignification</b>	
Consistence (%)	10
Temperature (°C)	110
Time (min)	30
% NaOH	1.4
% MgSO <sub>4</sub> ·7 H <sub>2</sub> O	0.5
Oxygen pressure (kg·cm <sup>-2</sup> O <sub>2</sub> )	6

After the oxygen delignification step, the pulp begins the chlorination step. This step will now require less of a chlorine load because of the reduction in the Kappa number (a decrease from 20.6 to 7) that occurred during the just completed oxygen delignification step. Table 4 shows the working conditions of the chlorination bleaching step.

**Table 4.** *Characteristic parameters of the chlorination step*

<b>Chlorine dioxide step</b>	
Consistence (%)	10
Temperature (°C)	70
Time (min)	60
% active chlorine	0.37·Kappa number

The wastewater obtained from this chlorination step was stored at -4°C. Analysis completed are summarized in Table 5

**Table 5.** *Characteristic parameters of the wastewaters from the chlorination step.*

<b>First laboratory generated pulp effluent</b>	
TOC (ppm)	306
COD (mg·L <sup>-1</sup> O <sub>2</sub> )	515
AOX (ppm)	27.7*
Color (c.u.)	250

\*the value correspond to 0.25 kg·t<sup>-1</sup> pulp

### Second laboratory generated paper pulp effluent

The effluents of this bleaching sequence were obtained as described before in the D step (chlorine dioxide bleaching step) from the AOD sequence with the exception that only the chlorine step is applied to the raw pulp. This single step was carried out under the same conditions as described previously in the chlorine dioxide bleaching step of the AOD sequence.

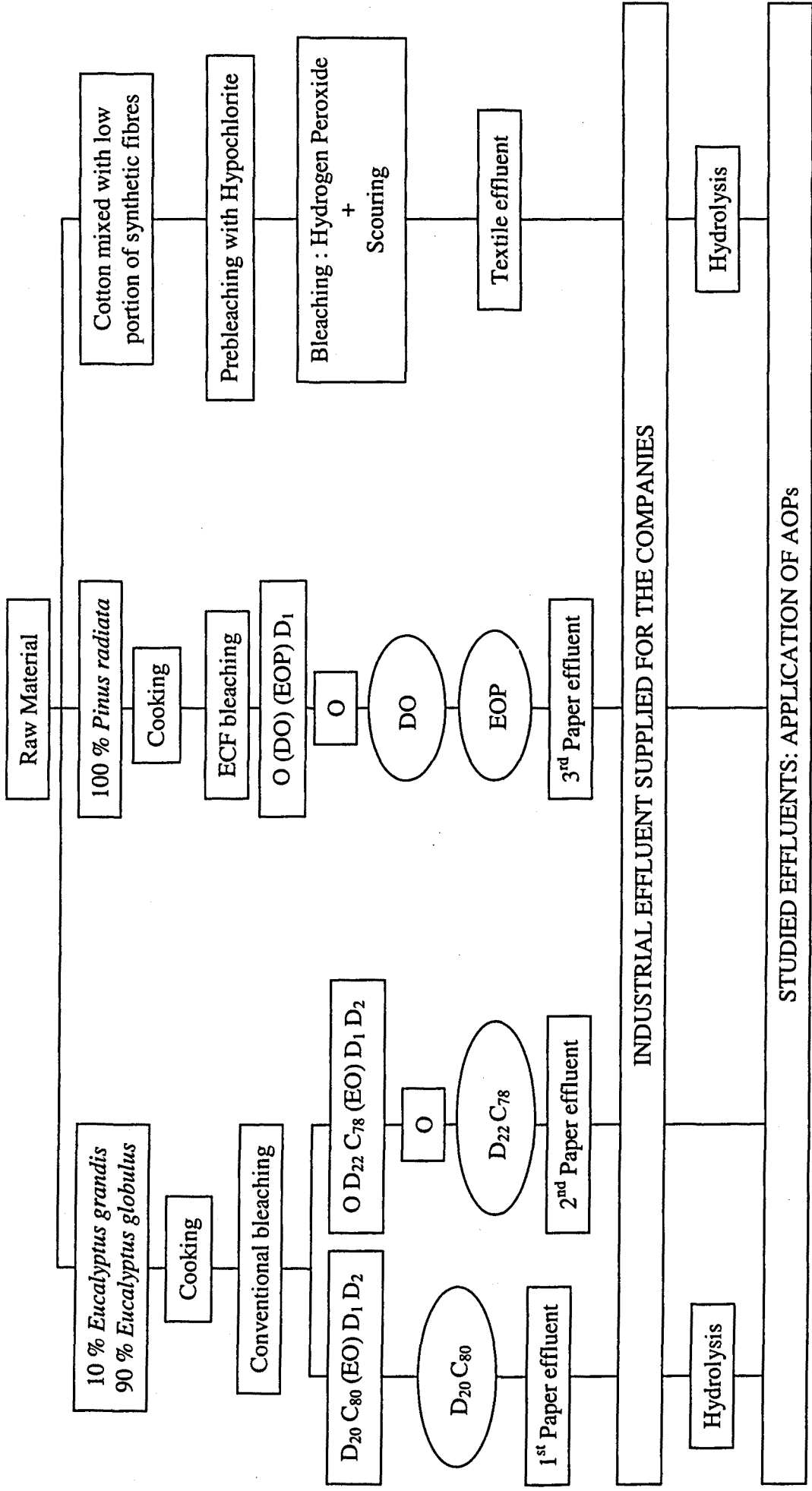
Table 6 summarizes characteristic parameters of wastewater obtained from this chlorination step. We would expect a higher contamination load in this effluent because, after the cooking process, nothing is done to the pulp until the chlorine dioxide bleaching step. The effluent was stored at  $-4^{\circ}\text{C}$ .

**Table 6.** *Characteristic parameters of the wastewaters from the chlorination step.*

<b>Second laboratory generated pulp effluent</b>	
<b>TOC (ppm)</b>	1380
<b>COD (<math>\text{mg}\cdot\text{L}^{-1} \text{O}_2</math>)</b>	3700
<b>AOX (ppm)</b>	69.8*
<b>Color (c.u.)</b>	7030

\*the value correspond to  $0.63 \text{ kg}\cdot\text{t}^{-1}$  pulp

**Industrial Effluents**



### First paper pulp effluent

The Kraft paper pulp effluent was obtained from a Spanish manufacturer. The firm kindly provided us the cooking and bleaching conditions. The classified raw material of 90% *Eucalyptus globulus* and 10% *Eucalyptus grandis* was used in the cooking step under the following processing conditions:

**Table 7.** *Characteristic parameters of the cooking process in a continuous industrial reactor.*

<b>Active alkali<sup>a</sup></b> (related to oven dry wood, expressed as % Na <sub>2</sub> O)	17
<b>Sulfidity<sup>b</sup></b> (%)	20
<b>Anthraquinone</b> (%)	0.05
<b>Liquor-to-wood ratio</b>	3:1
<b>*Residence time</b> (h)	4+5
<b>Maximum temperature</b> (°C)	170

<sup>a</sup> Na<sub>2</sub>S + NaOH; <sup>b</sup> Sodium sulfur/Active alkali.

\*Cooking time varies around one hour because with a continuous cooking process it is difficult to be more accurate.

The more important parameters of the pulp after the cooking process are the Kappa number (13) and the viscosity of the pulp (1100 cm<sup>3</sup>·g<sup>-1</sup>).

Immediately after the cooking process, the bleaching process was started. The pulp was then subjected to the conventional bleaching sequence of (D<sub>20</sub>C<sub>80</sub>)(EO)D<sub>1</sub>D<sub>2</sub>. It is a conventional sequence because the substitution of chlorine dioxide for chlorine was not 100 %. We collected this effluent from the first bleaching step where the substitution of Cl<sub>2</sub> by ClO<sub>2</sub> was 20%

The paper industry has found, that the best results and minimum cost in the chlorination step, are achieved when the percent substitution of chlorine by chlorine dioxide is around 20 %. A substitution rate of 60 % results in a better quality of the effluent, while remaining the same pulp quality. Economically, a 60 % substitution rate increases the cost substantially because chlorine dioxide is more expensive than the elementary chlorine. Table 8 shows the working conditions for the first bleaching step.

**Table 8.** *Characteristic parameters of the chlorination step.*

<b>Chlorine/Chlorine dioxide step</b>	
Consistence (%)	10
Temperature (°C)	60
Time (min)	30
ClO <sub>2</sub> (% substitution)	20

The parameters which characterize the pulp were not critical for this research because our studies are centered in the wastewaters. None the less, we found the quality of the pulp at the end all the bleaching process to be good and we found the viscosity after the chlorination step to be around 940 cm<sup>3</sup>·g<sup>-1</sup>.

The wastewater obtained from the paper pulp manufacturer was stored at -4°C and analyses done are summarized in Table 9.

As shown in the control parameters, the effluent presented high TOC, COD, and color values. For this reason a hydrolysis in basic media was carried out before we applied the processes under study. Dorica and Milosevich [Dorica, 1992, Milosevich and Hill, 1992] have reported the removal of organic chlorine, and the reduction of AOX discharge, from industrial bleach effluents using alkaline hydrolysis. The modified effluent was obtained by subjecting the wastewater, of the chlorine step, to hydrolysis with Ca (OH)<sub>2</sub> (at room temperature and pH 12 for 1 h). The results are summarized in Table 9.

**Table 9.** *Characteristic parameters of the wastewaters from the chlorination step before and after the hydrolysis treatment.*

<b>First industrial paper pulp effluent</b>		
	<b>Industrial effluent After hydrolysis</b>	
<b>pH</b>	1.33±0.06*	10.57±0.07*
<b>TOC (ppm)</b>	786±6*	441±8*
<b>COD (mg·L<sup>-1</sup> O<sub>2</sub>)</b>	1851±10*	1384±24*
<b>Color (c.u.)</b>	801±58*	197±25*

\*(n = 4, α= 0.05)



The hydrolysis of the effluent with  $\text{Ca}(\text{OH})_2$  eliminated 44 % of the TOC. Actually, not all the reduction in TOC is because of organic matter being mineralized; a significant portion of TOC is eliminated as a result of the precipitation process involved in the hydrolysis. The change in the color parameter was probably the most dramatic with a decrease of around 75 %

HPLC analysis done on the effluent and on a synthetic sample of 2,4-dichlorophenol, found similar retention times (around 19.7 minutes) in both samples. The industrial sample presented an area of 30% with respect to the 19.7 minutes retention time. Thus, the bleaching effluent could contain 2,4-dichlorophenol as was later corroborated with a GC-MS analysis.

Spectrophotometric analysis of the effluent allowed identification of the structure of some low molecular weight compounds present and confirmed the conclusions of the HPLC analysis. The mass spectra results, and the identified structures, are shown in section 6 (Papers 3, 4 and 5). All the substances identified displayed a high degree of chlorination which agrees with structures found and reported by other authors [Kringstad and Lindstrom, 1984, Ollis et al., 1991, Pérez et al., 2001]. Also, a large number of unidentified compounds, as well as some long chain acids, which appear in the chromatogram are not shown here.

### **Second paper pulp effluent**

The second Kraft paper pulp effluent, like the first paper effluent, was obtained from the same Spanish manufacturer. Although the raw material was of the same composition as the previous effluent (90% *Eucalyptus globulus* and 10% *Eucalyptus grandis*), and the cooking process was the same as with the first effluent, there were some important changes in the bleaching sequence. The firm supplied us with the new bleaching sequence and processing conditions.

Again, the pulp underwent a conventional bleaching sequence. The main difference with the first industrial effluent is that an oxygen delignification step was performed before the chlorination step. The bleaching sequence is  $\text{O}(\text{D}_{22}\text{C}_{78})(\text{EO})\text{D}_1\text{D}_2$ .

In order to reduce the Kappa number, an oxygen delignification step was performed, table 10 summarizes the processing conditions.

**Table 10.** *Characteristic parameters of the oxygen delignification step.*

<b>Oxygen delignification</b>	
Consistence (%)	12
Temperature (°C)	90
Time (min)	40
Alkali charge(kg·t <sup>-1</sup> NaOH)	9
Oxygen (kg·t <sup>-1</sup> O <sub>2</sub> )	8.5

After the oxygen delignification step, the pulp began the chlorination step with the rate of Cl<sub>2</sub> substitution by ClO<sub>2</sub> at 22%. This sequence will require less of a chlorine load because of the reduction of the Kappa number occurring in the previous oxygen delignification step. Table 11 shows the working conditions of the chlorination bleaching step.

**Table 11.** *Characteristic parameters of the chlorination step*

<b>Chlorine/Chlorine dioxide step</b>	
Consistence (%)	10
Temperature (°C)	60
Time (min)	30
ClO <sub>2</sub> (% substitution)	22

The parameters which characterize the pulp were not critical for this research because our studies were centered in the treatment of the wastewaters. None the less, we found the quality of the pulp at the end all the bleaching process to be good and we found the viscosity after the chlorination step to be around 850.

The wastewater obtained from the paper pulp manufacturer, during the chlorination step, was stored at -4°C. Table 12 summarizes the results of some of the analyses carried out.

**Table 12.** Characteristic parameters of the wastewater from the chlorination step.

Second industrial pulp paper effluent	
pH	1.74±0.08*
TOC (ppm)	537±9*
COD (mg·L <sup>-1</sup> O <sub>2</sub> )	1250±7*
Color (c.u.)	649±53*

\*(n = 4, α= 0.05)

As the control parameters show, the effluent presented lower TOC, COD, and color values than the first effluent. We would expect these results because, on this effluent, the hydrolysis pretreatment was not performed.

The structure of some low molecular weight compounds was determined by spectrometric analysis of the effluent. The mass spectra and the identified structures are shown in section 6 (Paper 6). All the substances found show a high degree of chlorination. This is in agreement with those structures found in the first paper pulp effluent and demonstrates that, although the hydrolysis treatment decreases the organic matter, it is not a selective treatment and the highly contaminated organic chlorine compounds are not totally eliminated after the treatment.

### Third paper pulp effluent

The last bleaching Kraft paper pulp effluent was obtained from a Chilean manufacturer. This effluent is clearly very different from the two effluents previously described. Besides the difference in raw materials and the different processing conditions, the effluent was obtained from a different bleaching step. The Chilean sample wastewater was produced during the first alkaline extraction in the bleaching sequence O(DO)(EOP)D<sub>1</sub>D<sub>2</sub>. The firm supplied all operating conditions.

The raw material (100% *Pinus radiata*, a softwood ) was used in the cooking step under processing conditions summarized in table 13.

**Table 13.** *Characteristic parameters of the cooking process in a continuous industrial reactor.*

<b>Active alkali<sup>a</sup></b> (related to oven dry wood, expressed as % Na <sub>2</sub> O)	20.6
<b>Sulfidity<sup>b</sup></b> (%)	33
<b>Liquor-to-wood ratio</b>	4:1
<b>*Residence time</b> (h)	4
<b>Maximum temperature</b> (°C)	162

<sup>a</sup>Na<sub>2</sub>S + NaOH; <sup>b</sup> Sodium sulfur/Active alkali.

\*the duration of the cooking process varies from one hour to one hour and 20 minutes because because it is difficult to be more accurate in a continuous cooking process.

The more characteristic parameters of the raw pulp are the viscosity and the kappa number. After the cooking process, we found them at 1090 cm<sup>3</sup>·g<sup>-1</sup> and 29 respectively. As could be expected, after this cooking process, the kappa number was higher than in the previous one, due to the raw material was a softwood. Consequently, we would expect there to be more bleaching reagent required and there to be a higher effluent contamination load.

On the other hand, the bleaching sequence begins with an oxygen delignification and the chlorination step is completed with a 100% chlorine dioxide substitution. This means a ECF sequence is involved and there will be less contaminant load than with conventional sequences.

The oxygen delignification step was carried out under the following processing conditions:

**Table 14.** *Characteristic parameters of the oxygen delignification step.*

<b>Oxygen delignification</b>	
Consistence (%)	10
Temperature (°C)	98
Time (min)	50
Oxygen (kg·t <sup>-1</sup> O <sub>2</sub> )	18

After the oxygen delignification step, the pulp begins the chlorination step with a 100 % substitution of  $\text{Cl}_2$  by  $\text{ClO}_2$ . The sequence will require less of a chlorine charge to be applied after the cooking processes because oxygen delignification has decreased the Kappa number. Table 15 shows the working conditions for the chlorination bleaching step.

**Table 15.** *Characteristic parameters of the chlorine dioxide step.*

Chlorine dioxide step	
Consistence (%)	10
Temperature (°C)	50
Time (min)	45
$\text{ClO}_2$ ( $\text{kg}\cdot\text{t}^{-1}$ )	16
$\text{ClO}_2$ (% substitution)	100

After the mandatory washing operation between bleaching steps, an alkaline extraction under the following conditions was performed:

**Table 16.** *Characteristic parameters of the alkaline extraction step.*

Alkaline extraction step	
Consistence (%)	10
Temperature (°C)	78
Time (min)	90
$\text{NaOH}$ ( $\text{kg}\cdot\text{t}^{-1}$ )	16
$\text{H}_2\text{O}_2$ ( $\text{kg}\cdot\text{t}^{-1}$ )	5
$\text{O}_2$ pressure ( $\text{kg O}_2\cdot\text{cm}^{-2}$ )	3

The typical pH of the water in the alkaline extraction step is around 11. However, when we checked the pH of the sample we were supplied, we found it to be around 7.2. The firm's explanation for this was that there was a mixing of this effluent with the effluent coming from the dioxide chlorination step, which is acid. The mixing of effluents is a fairly normal practice in the pulp and paper industries.

The wastewater obtained from the Chilean paper pulp manufacturer, from the alkaline extraction step, was stored at  $-4^\circ\text{C}$ . Analyses carried out are summarized in Table 17.

**Table 17.** *Characteristic parameters of the wastewaters from the chlorination step.*

<b>Third industrial paper pulp effluent</b>	
<b>pH</b>	7.2±0.1*
<b>TOC (ppm)</b>	487±4*
<b>COD (mg·L<sup>-1</sup> O<sub>2</sub>)</b>	1400±6*
<b>Color (c.u.)</b>	2100±60*
<b>AOX (ppm)</b>	58±1*
<b>Lignin and tannins (ppm)</b>	40±4*
<b>Toxicity (EC<sub>50</sub>)</b>	36.5±0.5

\*(n = 4, α= 0.05)

The effluent presented high color, COD, TOC values and a large amount of organochlorine phenols as shown by the AOX values and moderate acute toxicity.

Spectrometric analysis of the effluent allowed the identification of some low molecular weight compounds. The mass spectra and the identified structures are shown in Section 6 (Paper 7).

All the substances found showed a high degree of chlorination, as we would expect from the raw material, *Pinus radiata*. Besides, as expected syringol compounds were not found.

On the other hand, with our finding of 6-chlorovanillin, we were able to confirm those studies done by Yeber et al. [Yeber et al., 2000]. Also, we found a large number of unidentified compounds, and some long chain acids, in the chromatogram which are not shown here.

## **Textile effluent**

The bleaching textile effluent wastewater was provided by a Spanish manufacturer. The effluent comes from a hydrogen peroxide step in the bleaching process of raw cotton. In contrast to the paper pulp effluent, little information about the industrial processes involved with the textile industries was given to us. We assumed this was because the industry wishes to keep secret what concentrations of reagents are used and what their working conditions are.

In the main, the raw material is cotton that could be mixed with another kind of fiber, usually a synthetic one. The bleaching process, in this industry, is performed in two steps because the hydrogen peroxide bleaching step alone would not achieve the required bleaching grade. Although the hydrogen peroxide process by itself would be considered, a priori, the most favored from an environmental point of view, they must add another bleaching step that uses chlorine [Müller, 1992].

The first bleaching step is an impregnation of the raw material with hypochlorite at room temperature for 5 hours. The goal of this step is the elimination of organic and inorganic contaminants usually present in the virgin cotton. Unfortunately, this step is also the responsible for the appearance later of adsorbable organic halogen, (AOX) [Müller, 1992, Hickman, 1993, López, 1999].

Subsequently, a continuous process using hydrogen peroxide as bleaching agent is carried out. The use of this bleaching agent allows the simultaneous scouring and bleaching with the process carried out in an alkaline medium and at a high temperature.

It is essential to use an alkaline agent to activate the hydrogen peroxide. The pH should be kept around 10 by the addition of sodium hydroxide. One must keep in mind that to maximize the efficiency of this step, one must balance [Hickman, 1993] the alkaline agent concentration, the stabilizer concentration, the temperature and time.

Working at high temperatures leads to a decrease in the stability of the bleaching solution and to a consequent reduction in processing times. This leads to a reduction in the amount of oxygen in contact with the fiber while in the alkaline medium. Oxygen contacting the fiber in alkaline medium could negatively affect the fiber [Gähr and Schulz, 1995].

It is important to use a stabilizing product during this process because hydrogen peroxide is photocatalytically decomposed in presence of metal and oxides and could cause some damage to the cotton fibers [Shenai, 1984].

One must note that the effluent will ultimately end up with a wide range of compounds that originated from the different textile manufacturing processes beginning with the raw material and ending with the final product.

The wastewater obtained from the textile manufacturer during the hydrogen peroxide step was stored at  $-4^{\circ}\text{C}$ . Analyses carried out are summarized in Table 18.

As the control parameters show, the effluent presented high COD and TOC values. For this reason, a hydrolysis, in basic media, was carried out before the application of the studied processes. The modified effluent was obtained by subjecting the hydrogen peroxide step wastewater to hydrolysis with  $\text{Ca}(\text{OH})_2$  (pH 12 at room temperature for 1 h) which reduced all the parameters to the values shown in Table 18.

**Table 18.** *Characteristic parameters of the textile effluent from the hydrogen peroxide step, before and after the hydrolysis treatment.*

	Textile effluent	
	Industrial effluent After hydrolysis	
pH	10.38 $\pm$ 0.09*	12.14 $\pm$ 0.10*
TOC (ppm)	920 $\pm$ 5*	605 $\pm$ 9*
COD (mg $\cdot$ L $^{-1}$ O $_2$ )	2616 $\pm$ 29*	1669 $\pm$ 4*
Color (c.u.)	70 $\pm$ 6*	40 $\pm$ 8*

\*(n = 4,  $\alpha = 0.05$ )

The previous hydrolysis with  $\text{Ca}(\text{OH})_2$  reduce the TOC and COD parameters by about 35 %.

Spectrometric analysis of the effluent allowed the determination of the structure of some low molecular weight compounds. The identified structures are shown in Section 6 (Papers 9 and 10). It is possible that some of the main compounds found in the bleaching of cotton effluent by means GC-MS are the result of surfactant degradation by the bleaching agent, in this case, hydrogen peroxide. Our findings agree with those structures found and reported by other authors [López, 1999].

López [López, 1999] characterize two commercial surfactants that presented a structure with a nonylphenol polietoxilated base with etoxi groups. Additionally, a second minoritari compound was found, a fatty acid polietoxilate. That same researcher performed bleaching, in the laboratory, with the previously studied surfactants and, when the characterization of the wastewater was carried out, found products similar to



those we found by GC-MS. Consequently, the main compounds found in the hydrogen peroxide effluent appear to be coming from surfactant degradation.

The presence of a residual nonylphenol was not detected. But the existence of acids, aromatics, alcohols, or aldehydes by-products of the primary original compounds, leads one to conclude that the identified compounds came from the degradation of the surfactant (nonylphenol, fatty acid) during the cotton bleaching.

In regards to the lineal acids, all the series from C9 to C18 are identified. Thus, a priori, it is possible to believe that their source is the unsaturated fatty acid present in the surfactant.

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## SUMMARY

There is an ever increasing amount of research activities especially devoted to the solution of water pollution problems.

The pulp and textile industries are considered to be some of the largest polluters of all industries. The biggest problem with those industries consists in the polluted effluents discharged during the bleaching process because conventional biological treatments are not effective in treating these toxic pollutants. In these cases, the emerging technologies called Advanced Oxidation Processes (AOPs) represent an attempt to mineralize the contaminants by the *in situ* formation of hydroxyl radicals.

In order to determine the effectiveness of treating effluents with the hydroxyl radical we chose the photocatalytic and ozonation processes to treat bleaching pulp effluents generated in the laboratory. Our results demonstrated that the photocatalytic process could efficiently reduce the organic content in accordance with the Langmuir-Hinshelwood kinetic equation. Moreover, simultaneously combining photocatalysis and ozonation provided a synergistic effect that was superior in performance to that of applying the photocatalysis and ozonation processes sequentially.

Our tests with laboratory bleaching pulp effluents assumed that the hydroxyl radical was the proper oxidant to be use. An extensive study was undertaken using industrial wastewaters and different AOPs. TOC decay and treatment costs were the operative variables compared in the study in order to discover the benefits and shortcomings of each process.

It is imperative that the ozonation process decreases the treatment costs. The addition of iron ions to bleaching mill wastewater undergoing ozone/UVA treatment resulted in high rates of TOC removal (90%) and in a significant cost reduction (15%). Additionally, sequential processing (stirred iron, with or without light irradiation, followed by an ozonation stage) led to even better results. Similar results were obtained on the synthetic sample of 2,4-dichlorophenol (a compound typically found in paper pulp bleaching effluents) investigated.

We noticed that the photocatalytic process requires either a powerful light source or an improvement of the light utilization efficiency of the  $\text{TiO}_2$  catalyst, or maybe both, to be most effective. We tested two strategies: (a) A new experimental setup that used a high power light (125 W) to accelerate the reaction rate. AOX, acute toxicity, phenol and a GC-MS analysis led us to conclude that the chlorine organic compounds were efficiently eliminated from the treated wastewater. (b) The second approach consisted in

using titanium dioxide (TiO<sub>2</sub>)-coated waveguides. This approach increases the light utilization efficiency of the TiO<sub>2</sub> catalyst with the aim of improve the reactor's design.

The last process that was tested involved the addition of Fenton reagent to the bleaching pulp and textile effluents in conjunction with either artificial or solar light. The degradation of the organic contents was successfully performed at pH = 3.

The first study was performed on bleaching pulp effluent. The approximate function of the system, as assessed by the experimental design, showed that initial non-optimum concentrations of the Fenton reagent were detrimental to the process because of competitive reactions of the Fenton reagent with oxidative species.

On the other hand, temperature markedly increased the reaction rates, even without light irradiation. The improvement in TOC removal was particularly significant when the reagent ratios were not optimal. A decrease in cost around 80% is possible by just increasing the temperature from 25°C to 40°C. Moreover, solar light reduced the total cost of a two hour treatment by up to 70 % and efficiently removed the chlorophenolic compounds as shown by GC-MS analysis.

The second study performed on textile wastewater corroborates the importance of the temperature parameter and the utility of solar energy.

In summary, all AOPs tested displayed the capability to degrade the organic components of bleaching Kraft mill and textile mill effluents under suitable experimental conditions.

## RESUM

Les activitats de recerca destinades a la solució dels problemes de contaminació de les aigües estan patint un fort increment en els darrers anys.

Entre les indústries més contaminants, cal esmentar la tèxtil i la paperera, i més concretament, els efluent provinents d'etapes de blanqueig. Quan els tractaments biològics convencionals d'aquests efluent contaminants no són efectius, la utilització de tecnologies emergents, tals com els processos d'oxidació avançada (AOP's), basats en la formació *in situ* de radicals hidroxil, es mostra adient.

Amb l'objectiu de provar la viabilitat de tractar efluent contaminants amb el radical hidroxil, vàrem triar l'ozonització i la fotocatàlisi per abordar efluent de blanqueig de pastes papereres generats en el laboratori. Aquesta prova mostrà que la fotocatàlisi pot reduir eficientment el contingut de carrega orgànica tot seguint una equació cinètica de Langmuir-Hinshelwood. A més, la combinació simultània de fotocatàlisi i ozonització produí un efecte sinèrgic que millorava el rendiment respecte al cas d'aplicar ambdós AOP's de manera seqüencial.

Tot i assumint que el radical hidroxil era l'oxidant adequat, planificàrem un extens estudi, fent servir aigües residuals industrials i distint AOP's. La disminució del TOC i el cost en el tractament varen ésser els paràmetres contrastats en els distint estudis, amb l'objectiu de descobrir els principals avantatges i inconvenients de cada procés.

El procés d'ozonització requeria disminuir el seu cost. La presència d'ions ferro en el procés ozó/UVA va aconseguir la reducció d'un 90% de TOC conjuntament amb una disminució del 15% en el cost. L'ús seqüencial de tractaments genera millors resultats (addició de ferro amb o sense llum, seguit per una etapa d'ozonització). Conclusions similars es varen obtenir en treballar amb una matriu sintètica de 2,4-diclorfenol (compost trobat usualment en els efluent de blanqueig de pasta de paper).

Referent a la fotocatàlisi, s'ha posat de manifest la necessitat d'utilitzar una font de llum potent i/o la millora de l'eficiència de la llum incident en el catalitzador de TiO<sub>2</sub>. En aquest sentit vàrem provar dues vies:

(a) la utilització d'un nou muntatge experimental amb una font de llum de 125 W. Determinacions d'AOX, toxicitat aguda, fenols i de GC-MS ens van portar a concloure que els compostos orgànics de clor eren eliminats eficientment en l'aigua residual.

(b) la utilització de guies d'ones recobertes de  $\text{TiO}_2$ . Solució que permet augmentar l'eficiència amb la que el catalitzador aprofita la llum incident per tal de millorar el disseny de reactors fotocatalítics.

L'últim procés provat, el reactiu Fenton, en presència de llum solar o artificial, es va aplicar a la degradació d'efluents de blanqueig tèxtils o paperers. La degradació del contingut de càrrega orgànica d'aquests efluents s'assolia preferentment a  $\text{pH} = 3$ .

El primer estudi es realitzà sobre un efluent de blanqueig de pastes de paper. La funció aproximada del sistema, estimada a partir del disseny experimental, mostrà que concentracions inicials inadequades de reactiu Fenton afectaven negativament al procés, a causa de reaccions competitives entre aquest i altres espècies oxidatives.

Així mateix, la temperatura augmentà clarament les velocitats de la reacció, inclús sense presència de radiació. La millora en la disminució del TOC és particularment significativa quan les proporcions de reactiu Fenton són inadequades (en passar de  $25\text{ }^\circ\text{C}$  a  $40\text{ }^\circ\text{C}$  es pot aconseguir una reducció en el cost de l'ordre del 80%).

Per altre banda, la llum solar aconsegueix reduir fins un 70 % el cost total d'un tractament de dues hores de durada. L'anàlisi de GC-MS constata l'eliminació dels compostos clorfenòlics.

Un segon estudi sobre un efluent tèxtil corroborà la gran importància de la temperatura i de la presència de llum solar.

En resum, tots els AOP's provats mostren, sota condicions experimentals adequades, la capacitat de degradació del contingut orgànic present en efluents de blanqueig procedents d'indústries papereres i tèxtils.

## RESUMEN

Las actividades de investigación destinadas a resolver los problemas de contaminación en las aguas están sufriendo un fuerte incremento en los últimos años.

Entre las industrias más contaminantes cabe mencionar la papelera y la textil. En concreto, los efluentes procedentes de las etapas de blanqueo. Cuando los tratamientos biológicos convencionales de los efluentes contaminados no son efectivos, la utilización de tecnologías emergentes, como son los procesos de oxidación avanzada (AOPs), basados en la formación *in situ* de radicales hidroxilo, se muestra adecuada.

Con el objetivo de probar la viabilidad del tratamiento de efluentes contaminantes con el radical hidroxilo, elegimos las técnicas de fotocátalisis y ozonización para tratar efluentes de blanqueo de pastas papeleras generados en el laboratorio. Los resultados obtenidos mostraron que la fotocátalisis podía reducir eficazmente el contenido de carga orgánica, siguiendo una cinética de Langmuir-Hinshelwood. Asimismo, la combinación simultánea de fotocátalisis y ozonización producía un efecto sinérgico que mejoraba el rendimiento respecto al alcanzado cuando ambos AOPs se aplicaban de forma secuencial.

Asumiendo que el radical hidroxilo era el oxidante adecuado se planificó un extenso estudio, utilizando aguas industriales residuales y distintos AOPs. La disminución en el TOC y en el coste del tratamiento fueron los parámetros contrastados en los distintos estudios con el objetivo de descubrir las principales ventajas e inconvenientes de cada proceso.

El proceso de ozonización requería disminuir su coste. La presencia de iones hierro en el proceso ozono/UVA alcanzó una reducción del 90% de TOC conjuntamente con una disminución de un 15% en el coste. El uso secuencial de tratamientos genera mejores resultados (adición de hierro con o sin luz, seguido por una etapa de ozonización). Resultados similares se obtienen al tratar una matriz sintética de 2,4-diclorofenol (uno de los componentes típicos de los efluentes de blanqueo de pasta de papel).

Por lo que hace referencia a la fotocátalisis, se puso de manifiesto la necesidad de utilizar una fuente de luz potente y/o mejorar la eficiencia con que el catalizador de  $\text{TiO}_2$  aprovecha la luz incidente. En este sentido se probaron dos vías:

(a) la utilización de un nuevo montaje experimental que empleaba una fuente de luz de 125 W. Determinaciones de AOX, toxicidad aguda, fenoles y de GC-MS nos llevaron a la conclusión de que los compuestos orgánicos clorados eran eficientemente eliminados en el agua residual tratada.



(b) la utilización de guías de ondas recubiertas de  $\text{TiO}_2$ . Solución que permite aumentar la eficiencia con que el catalizador de  $\text{TiO}_2$  aprovecha la luz incidente para mejorar en el diseño de reactores fotocatalíticos.

El último proceso ensayado, el reactivo Fenton, conjuntamente con luz solar o artificial, se aplicó a la degradación de efluentes de blanqueo de industrias textiles o papeleras. La degradación del contenido de carga orgánica de estos efluentes se alcanzaba preferentemente a  $\text{pH} = 3$ .

El primer estudio se realizó sobre un efluente de blanqueo de pastas papeleras. La función aproximada del sistema, estimada a partir del diseño experimental, muestra que concentraciones iniciales inadecuadas de reactivo Fenton son perjudiciales para el proceso, a causa de reacciones competitivas entre éste y otras especies oxidativas.

Asimismo, la temperatura aumentó claramente las velocidades de reacción, incluso en ausencia de radiación. La mejora en la reducción del TOC es claramente significativa cuando las proporciones de reactivo Fenton son inadecuadas (elevando la temperatura de  $25\text{ }^\circ\text{C}$  a  $40\text{ }^\circ\text{C}$  se puede conseguir una reducción en el coste del orden de un 80%).

Además, la luz solar consiguió reducir hasta un 70% el coste total de un tratamiento de dos horas de duración. El análisis de GC-MS constató la eficiente eliminación de compuestos clorofenólicos.

Un segundo estudio, sobre un agua residual textil, corroboró la importancia de la temperatura y de la utilización de energía solar.

Para concluir, podemos decir que todos los AOPs ensayados muestran, bajo determinadas condiciones experimentales, la capacidad de degradar los compuestos orgánicos presentes en efluentes de blanqueo procedentes de industrias papeleras o textiles.

## SOUHRN

V posledních letech dochází ke značnému nárůstu výzkumných aktivit v oblasti ochrany životního prostředí věnujících se čistotě vody. Mezi největší znečišťovatele patří již tradičně papírenský a textilní průmysl.

Jelikož běžně užívané konvenční metody čištění nejsou vždy plně funkční, dostává se velká část kontaminovaného odpadu, vznikajícího především během procesu bělení dřevěné kaše v papírnách, volně do okolního prostředí. V takovýchto případech se pak jeví podstatně efektivnější využití moderních technologií AOP (pokročilé oxidační procesy), založených na In situ tvorbě hydroxylových radikálů.

Pro porovnání účinnosti těchto čistících postupů jsme zvolili metody fotokatalýzy a ozonizace, aplikované na bělicí odpad získaný laboratorním způsobem. Výsledky prokázaly, že fotokatalýza může efektivně snížit obsah organické kontaminace, v souladu s kinetickou rovnicí – Langmuir - Hinshelwood. Zároveň, při kombinaci fotokatalýzy a ozonizace, dochází k značnému zlepšení dosažených výsledků v porovnání s jejich nezávislou aplikací.

Laboratorní testy potvrdily správnost výběru hydroxylových radikálů jako oxydantů. Rozsáhlý výzkum byl následně zaměřen na různé AOP procesy a jejich aplikaci na reálné průmyslové odpadní vody. V průběhu této studie byly porovnávány 2 hlavní parametry – snižování TOC (obsah organického uhlíku) a cena, na jejichž základě byly následně hodnoceny obě použité metody.

Důležitým úkolem bylo snížení ceny u ozonizační metody. Přidáním iontů železa do procesu ozon/UVA bylo dosaženo až 90% snížení TOC při 15% redukci nákladů. Ještě lepších výsledků jsme dosáhli při rozdělení procesů do posloupnosti jednotlivých kroků (přidáním iontů Fe za/bez světla, a následnou ozonizací). K podobným výsledkům jsme též dospěli aplikací metody na syntetický roztok 2,4-dichlorofenolu.

Pro zvýšení rychlosti fotokatalýzy bylo nutno použít výkonnějšího zdroje osvětlení, anebo zajistit lepší využití osvětlení stávajícího. Z tohoto hlediska jsme k problému přistupovali dvěma způsoby: (a) Použitím silnějšího zdroje světla – 125W pro urychlení průběhu reakce. AOX, analýza toxicity, fenolu i GC-MS (plynová chromatografie – látková spektrometrie) ukázaly efektivní eliminaci chlorových organických sloučenin z čištěné vody. (b) Usměrněním světelného záření pomocí speciálních vodičů pokrytých TiO<sub>2</sub>. Řešení umožňuje zvýšit využití stávajícího osvětlení katalyzátorem TiO<sub>2</sub> s ohledem na jeho praktickou aplikaci při návrhu fotokatalytických reaktorů.

Poslední metodou ke snížení kontaminace aplikovanou na odpadní vodu bělicího procesu papírenského a textilního průmyslu, bylo použití reaktantu Fentonu při slunečním i umělém osvětlení. Nejlepších výsledků se dosáhlo při hodnotě pH=3.

První experimentální studie byla provedena s odpadní vodou vznikající při procesu bělení dřevěné kaše v papírenském průmyslu. Řídící funkce systému získaná experimentálním způsobem nám ukázala, že nepřiměřené vstupní koncentrace reaktiva Fentonu snižují účinnost celého procesu, vinou svých souběžných reakcí s oxidativními částicemi.

Na druhou stranu se však ukázalo, že nárůst teploty výrazně urychluje rychlost dané reakce, a to i při absenci světelného záření. Toto zlepšení redukce TOC bylo nejvíce patrné při neoptimálním poměru použitých reaktantů. Pouhým zvýšením teploty z 25°C na 40°C bylo dosaženo až 80% snížení nákladů. Mimoto, použití solárního světla vedlo navíc až k 70% úspoře při 2 hod. procesu a zároveň efektivnímu odstranění chlorofenolových složek, což následně potvrdila analýza GC-MS.

Druhá studie prováděná s odpadní vodou z textilního průmyslu potvrdila důležitost teploty, jakož i význam solárního záření.

Závěrem lze shrnout, že všechny testované AOP potvrdily, v determinovaných laboratorních podmínkách, schopnost snížení koncentrace organických nečistot v odpadu z papírenského i textilního průmyslu.