

High frequency ultrasound as a pre- or a post-oxidation for paper mill wastewaters and landfill leachate treatment

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Abstract

The ultrasonic process is investigated to remove refractory pollutants. The particular case of sodium pentachlorophenate is studied as a model molecule and several raw paper mill wastewaters and a landfill leachate are chosen as real industrial wastewaters. As the sonication requires a lot of energy, it is investigated as a pre- or a post-treatment in combination with biodegradation. For that, global indicators of the environmental pollution (COD, TOC, toxicity and biodegradability) are examined. The results show that ultrasound can decrease toxicity and enhance biodegradability. The amount of energy supplied and the position of the chemical treatment (pre- or post-treatment) are discussed.

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1. Introduction

For several decades, ultrasonic process is considered as a new possibility in wastewater treatment field. It is able to remove pollutants through the production of radicals in the bubble of cavitation that can react with refractory compounds. A lot of studies investigated the process feasibility with synthetic aqueous solutions containing model pollutants. In the case of one compound, the concentration in the target pollutant and the first intermediates can be measured and their reaction kinetics can be modelised [1–4]. But, as ultrasonic irradiation leads to a lot of products, it is almost impossible to identify all of them and to complete the mass balance. In the case of mixture of several pollutants, the follow-up of the initial compounds is still possible but modelling the reaction kinetics becomes very tricky. Due to the complex properties of a real wastewater and the multitude of products formed by sonication, studies are very scarce and are not all in accordance [5–7]. Investigators are now confronted to the difficulty of studying a real effluent.

In addition, if chemical oxidation processes are of great interest with the toxic compounds, they are very expensive to totally mineralise a complex wastewater. The biological processes are cheap, but they are powerless to oxidise the toxic compounds. So the combination of chemical and biological processes can be an interesting option. This publica-

tion is devoted to the oxidation of several industrial wastewaters by combined chemical and biological processes.

As sonication of synthetic solutions is still necessary to understand sonolytic mechanisms and reaction kinetics, the first part of this work is devoted to the ultrasonic degradation of sodium pentachlorophenate (NaPCP) solutions. Through chemical oxygen demand (COD), total organic carbon (TOC), biological oxygen demand after 5 days (BOD₅) and toxicity measurements, the efficiency of the process as a pre-oxidation step before a classical biological treatment is discussed. The second part of the study investigates the sonication of three different raw paper mill wastewaters. Ultrasound is then used as a pre-oxidation before a biological treatment. The last part of this paper deals with the sonication of a biologically pre-treated landfill leachate. The ultrasonic process is then considered as a post-treatment.

2. Material and measurements

2.1. Setup and wastewaters studied

The experimental setup (Fig. 1) was composed of an ultrasonic transducer (40 mm diameter) connected to a high frequency generator (500 kHz, 100 W) and fixed to the bottom of a 1 l reactor vessel. The reactor was closed with a cap in order to avoid emission of solution and to minimise the loss of pollutant by evaporation. A glass jacket allowed the circulation of a cooling fluid that maintained the temperature

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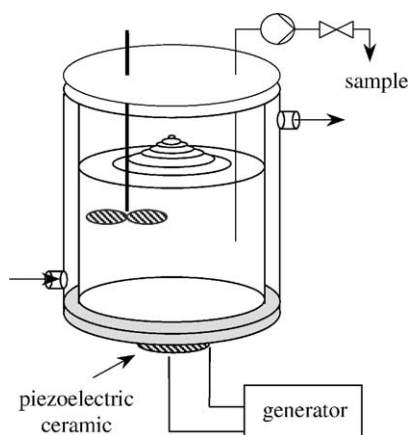


Fig. 1. Experimental setup.

at $20 \pm 2^\circ\text{C}$ during the whole sonication. All experiments were conducted in batch conditions with a solution volume from 250 to 650 ml and a dissipated power, evaluated with the calorimetric method, between 55 and 65 W.

Chlorophenolic aromatic compounds were used as model pollutants because they exhibit an important bioresistance in terms of lag period and reaction rate. With a 20 days BOD study, Hu and Yu [8] indicated that the bioresistance of these compounds increases with the number of chlorine atoms and that in the *meta* position the chlorine atom is particularly toxic. Thus our experiments were carried out with sodium pentachlorophenate (NaPCP) aqueous solutions with an initial concentration of 0.1 or 1 mM. Pentachlorophenol was dissolved in a basic solution. The pH was brought to 12 by adding sodium hydroxide pellets. The pH was then adjusted to 7 with phosphoric acid.

Real industrial wastewaters are issued from the bleaching process of a paper mill (CELLURHONE, Tarascon, France). They are produced by the washing of the pulp and contain various chlorophenolic compounds which are refractory to conventional treatments. Three different paper mill wastewaters were sonicated. Their properties are presented in Table 1. The first one (no. 1) was a basic wastewater concentrated by ultrafiltration (with a molecular weight cut off of 3000 Da)

with a COD about 15 g/l. The second one (no. 2) was also a basic wastewater whose COD is only about 3 g/l because it was not concentrated. Its inorganic carbon concentration is high (205 mg C/l). The last one (no. 3) was an acidic wastewater with a COD about 2 g/l and without inorganic carbon. All of them were filtered with glass filters (2 μm pore size) before sonication in order to remove suspended matter. The bleaching step of the pulp consists in a chlorination in an acidic medium that forms aromatic chlorinated compounds which are extracted with a sodium hydroxide solution in a second step. It means that the acidic wastewater contains low molecular weight compounds whereas basic ones are very concentrated in high molecular weight species.

The leachate is issued from a 20 years old municipal landfill. It has been treated with a biological oxidation at the outlet of the landfill in order to remove the biodegradable fraction. So, it remains in the treated leachate refractory compounds that have resisted to the biological treatment. The low biodegradability of the wastewater is confirmed by the very low BOD₅/COD ratio (Table 1). The exact composition of the leachate is unknown but a literature survey [9] suggests that it contains aromatic organic compounds, halogenated ones, humic substances, heavy metals, ammonia and also a high concentration in inorganic carbon.

2.2. Measurements and calibration curves

2.2.1. Concentration, oxidation and mineralisation measurements

NaPCP concentration was monitored by HPLC (Waters 600E Millipore) with an Alltech Spherisorb ODS2 column. The mobile phase was an acetonitrile–water (70–30) mixture and the detection was achieved by measuring absorbance at 254 nm. Hydrogen peroxide concentration was measured by using analytical test strips (MERCK).

COD and TOC are two appropriate ways to evaluate, respectively, the global oxidation and mineralisation rate of the organic mixtures. The first one leads to the amount of the oxidisable matter and was undertaken with COD ampoules (HACH) in accordance with Standard Methods. This measurement consists in the oxidation of the organic matter

Table 1
Properties of the synthetic and industrial wastewaters studied

Wastewaters	NaPCP	Concentrated basic paper mill (no. 1)	Basic paper mill (no. 2)	Acidic paper mill (no. 3)	Landfill leachate
Concentration or properties	1 mM	Large molecules (>3000 Da)	Large and small molecules	Small molecules	–
Colour	Colourless	Dark brown	Dark brown	Dark brown	Dark yellow
pH	7	9	9	6	8
TOC (mg C/l)	73	n.d. ^a	1380	934	217
COD (mg O ₂ /l)	160	15,000	3000	2000	600
BOD ₅ (mg O ₂ /l)	inhibition = –58	n.d.	n.d.	220	0
BOD ₅ /COD	n.d.	n.d.	n.d.	0.11	0
Inorganic carbon (mg C/l)	n.d.	n.d.	205	4	high
Toxicity (%)	>99	>90	45	60	10

^a Not determined.

in a sulphochromic medium. Chloride ions with a concentration higher than 1.5 g/l interfere with the measure. In this case, the value of the COD may be overestimated. TOC was measured with a LABTOC analyser and a CO₂ detector Hartmann and Braun Uras 10E.

2.2.2. Toxicity measurements

The toxicological test used (AFNOR T-90-320 norm) evaluates the inhibition of the bioluminescence emitted by bacteria called *Vibrio fischeri* when they are exposed to the pollutant. These bacteria emit light and the luminous intensity is related to the metabolism of the bacteria. Aliquots of bacteria suspensions (200 µl) containing nutritive compounds were added to the samples (200 µl) whose pH was adjusted between 5.5 and 8.5. Bioluminescence intensity was measured during 10 s with a luminometer (PRODEMAT Lucy) before and after a 5 min exposure to the pollutant. These conditions have been optimised with preliminary experiments [10]. The toxicity is then calculated and expressed in percent of bioluminescence inhibition. The sample can be considered as non-toxic when this value is less than 20%. Beyond 80% the test saturates, it is not sensitive to variations. Hence the samples must be diluted.

To evaluate the test sensibility, calibration curves were made with standard solutions of NaPCP, tetrachlorobenzoquinone (TCBQ), tetrachlorohydroquinone (TCHQ), hydrogen peroxide and nitrate ions. These species are produced during sonication of pentachlorophenolate aqueous solutions. Fig. 2 reports their toxicity as a function of their concentration. These results confirm the high toxicity of NaPCP whose critical concentration is about 10⁻⁶ M. TCBQ and H₂O₂ are less toxic species. Their critical concentration is between 0.05 and 0.5 mM. TCHQ and nitrate ions are non-toxic towards bacteria for concentrations less than 1 mM.

2.2.3. Biodegradability measurement

The second biological measurement using activated sludge allows to evaluate the biological treatability of the

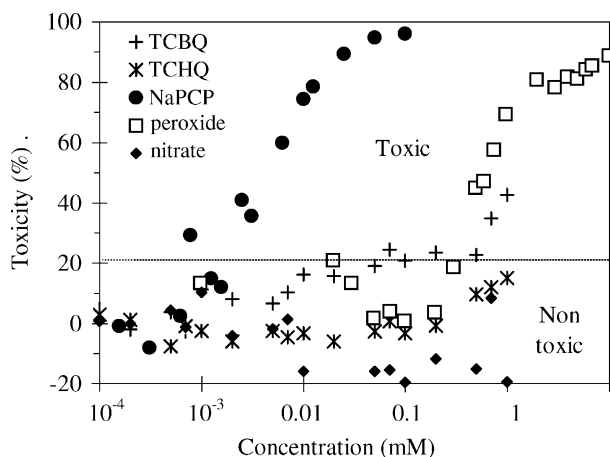


Fig. 2. Toxicity of standard solutions of NaPCP, TCBQ, TCHQ, hydrogen peroxide and nitrate ions as a function of their concentration.

wastewater before or after the chemical oxidation. Activated sludge is a mixture of several species, so BOD measurement is not as sensitive to the toxic compounds as tests using specific bacteria. This fact has been demonstrated by Hao et al. [11] who treated a trinitrotoluene red water from an explosive manufacturing by wet oxidation and found that the treated wastewater was significantly more toxic on selected cultures (*Acinetobacter*, *Nitrosomonas*) than on activated sludge. Thus, these two measurements are complementary. The BOD₅ was determined in accordance with the AFNOR T-90-103-1 norm with the help of an Oxitop[®] (WTW). Samples (100 ml) whose pH was previously adjusted to 7 were placed in 365 ml bottles in the presence of a saline solution (165 ml) containing an aerobic biological seed (20 ml). This seed was sampled at the outlet of a wastewater purification plant and was non-acclimated to the pollutants studied. These solutions were completed to 365 ml with deionised water. Some NaOH pellets are placed at the top of the bottles in order to absorb the CO₂ emitted by bacteria respiration. Then, bottles are sealed under air and kept at 20 °C under continuous stirring. The dioxygen consumption was indirectly evaluated by the measurement during 5 days of the pressure fall within the bottles. Each sample was duplicated. Moreover, a “control” whose 5 days respiratory activity was between 2 and 8 mg O₂/l was made without any pollutant. Then the BOD₅ was calculated with the difference of dioxygen consumption between the sample and the control.

2.2.3.1. Biodegradability measurement in industrial wastewaters. As the paper mill wastewaters and the leachate are biodegradable, the measurement was applied in the conditions described over there. The results are expressed directly with BOD₅. The BOD₅ of the acidic paper mill is about 220 mg O₂/l and the value measured with landfill leachate is equal to 0.

2.2.3.2. Biodegradability measurement in synthetic solution of NaPCP. If the toxic chlorinated compound (NaPCP, TCHQ, TCBQ) is used as the sole carbon source or if there is only mineral species (peroxide), the biodegradability cannot be evaluated with this method because the biological activity is too weak or totally inhibited. For example, a preliminary measure realised only with NaPCP (1 mM) and seed had exhibit a respiratory activity of 2 mg O₂/l, less than the control. Thus in these cases, a specific method was developed. A nutritive solution of glucose (150 mg/l) and glutamic acid (150 mg/l) was added as baseline. A “reference” containing only the seed and this nutritive solution was made and its BOD₅ was (216 ± 10) mg O₂/l (Table 2). Adding the nutritive compounds to the sample permits to quantify the inhibitory effect of the pollutant on the biological activity. The results are expressed in term of inhibition: BOD₅ inhibition = BOD₅(sample+NS) - 216.

If the BOD₅ value of the sample with the nutritive compounds is above the reference value (216 mg O₂/l), the sample is considered as biodegradable. If it is equal it is

Table 2
BOD₅ and BOD inhibition of NaPCP, TCBQ, TCHQ and hydrogen peroxide (1 mM)

Solution	BOD ₅ (mg O ₂ /l)	BOD ₅ inhibition or reduction (mg O ₂ /l)
NS ^a	216 ± 10	Not applicable
NS + NaPCP (1 mM)	168 ± 6	-48
NS + peroxide (1 mM)	198 ± 12	-18
NS + TCHQ (1 mM)	248 ± 15	+32
NS + TCBQ (1 mM)	253 ± 9	+37

^a Nutritive solution.

non-biodegradable and if it is below it is non-biodegradable and inhibiting. The BOD₅ measurement was undertaken in presence of standard solutions of NaPCP, TCBQ, TCHQ and H₂O₂ (Table 2). NaPCP compound is non-biodegradable and a significant inhibitory effect can be observed with a high concentrated solution (1 mM). In this case, the BOD of the NaPCP with nutritive compounds is (168 ± 6) mg O₂/l. That means that the inhibition due to NaPCP is about -48 mg O₂/l which represents 25% of the biological activity. TCBQ and TCHQ seem biodegradable by this activated sludge. Indeed, BOD₅ values are above the reference one.

Experiments carried out with hydrogen peroxide reveal that the presence of this compound interferes with the measurement and the BOD value is minimised. Due to the enzymatic catalase reaction, peroxide may be disproportionated into molecular oxygen and water. This resulting oxygen is then used by micro-organisms for their aerobic metabolism and reduces the BOD value. The experiments show that with a 1 mM solution, the reduction is about 18 mg O₂/l. It can be noted that the theoretical reduction due to the oxygen produced by hydrogen peroxide transformation is equal to 16 mg O₂/l (0.5 mol O₂ is formed per mole of H₂O₂ consumed).

On top of this interference, a toxic effect can exist with high concentration. The detrimental effect of hydrogen peroxide was observed by Carberry and Benzing [12] during the hydrogen peroxide pre-oxidation of pentachlorophenol, toluene and trichloroethylene solutions. High residual levels of hydrogen peroxide which adversely affected the bio-activity were detected. Peroxide concentrations in the 10–1000 mg/l range have been found to inhibit bacteria growth and higher concentrations destroy the micro-organisms [13]. Recent results show that, after an adaptation of the microbial organisms, a concentration of 100 mg/l can be used without any problem [14].

2.2.4. Biodegradability and toxicity measurements limitations

Biological measurements include acclimated or unacclimated seed. Literature points out that the acclimation of the activated sludge system can result in different and even opposite conclusions. If the oxidative pathways are different, the species obtained by the chemical oxidation may not be the same that metabolic intermediates formed by

bio-oxidation. In this case if the seed has been previously acclimated, the initial chlorophenolic compound is easily accepted but intermediate compounds due to chemical oxidation could be more toxic and more difficult to digest by these acclimated micro-organisms. This negative effect of bacteria acclimation was observed by Hu and Yu [8] and Bowers et al. [15]. Contrary, Lee and Carberry [16] found that if the micro-organisms were acclimated to the parent compound as pentachlorophenol they degraded more easily the samples after a partial chemical oxidation. Due to these contrary results, we chose to work with unacclimated sludge.

Concerning toxicity assessment, the literature points out that some species are more sensitive than others. So, results must be interpreted more qualitatively than quantitatively. For example, Thomsen and Kilen [17] compared two kinds of selected bacteria and observed that *Nitrosomas* is more sensitive than *Nitrobacter* even if qualitatively results are very close.

3. Results

3.1. Synthetic sodium pentachlorophenate solutions

3.1.1. Pollutant concentration and oxidation rate

Sodium pentachlorophenate sonication is studied for several years in the laboratory. The ultrasonic irradiation of an air-equilibrated aqueous solution of NaPCP at 1 mM is reported in Fig. 3. Pentachlorophenol is in aqueous solution as its sodium salt form (sodium pentachlorophenate) which restricts its entrance in the cavitation bubbles. So, the major degradation mechanism is the hydroxyl radical oxidation with the cleavage of the C–Cl bonds. This mechanism is confirmed by the detection of TCBQ and TCHQ as first intermediates. Chloride radicals are liberated, reduced to chloride ions that can react with hydronium ions (from water decomposition) and form hydrochloric acid. These

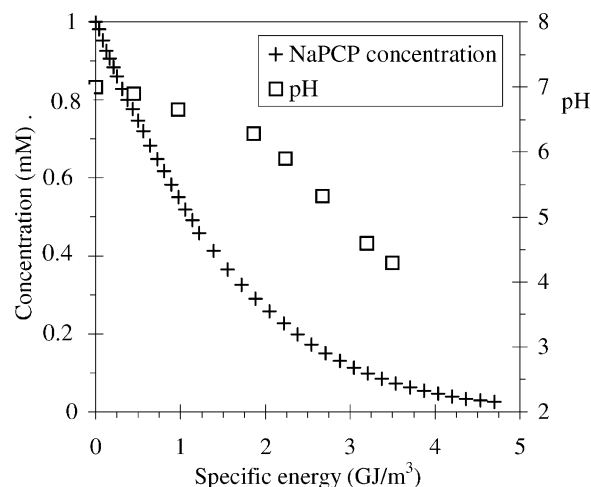


Fig. 3. NaPCP concentration and pH vs. specific energy during sonication of a 1 mM solution of sodium pentachlorophenate.

Table 3
TOC, COD and BOD₅ during sonication of a 1 mM NaPCP solution and BOD₅ during sonication of water

Energy (GJ/m ³)	NaPCP solution			Water (BOD ₅ inhibition or reduction (mg O ₂ /l))
	TOC (mg C/l)	COD (mg O ₂ /l)	BOD ₅ inhibition (mg O ₂ /l)	
0	73	148	−48	0
0.9	–	135	−46	−7
2.7	55	120	−54	–
3.6	47	125	−67	−14
4.5	54	108	−7	−40

acidic conditions would need readjustment before a further biological treatment. The decrease of NaPCP concentration has been modelled previously [3,18]. According to experimental results, the model demonstrates clearly that in our experimental conditions the disappearance of NaPCP depends on the power density and not on the intensity (power emitted per unit area of the transducer). That is why all results are expressed vs. the specific energy supplied (GJ/m³).

Sonication of NaPCP leads to products formation. TCBQ, TCHQ and organic acids were identified as intermediates products and CO₂ as ultimate one. Sonication in aqueous medium leads also to the formation of hydrogen peroxide due to the recombination of hydroxyl radicals. It was found a formation rate of hydrogen peroxide about 0.35 mol/GJ. The formation of nitrate ions during sonication under air have also been demonstrated by several authors [19–21]. Nitrous oxide is formed firstly and is transformed into NO then into nitrite and nitrate ions.

3.1.2. Overall oxidation and mineralisation

The overall oxidation and mineralisation extent were evaluated with 1 mM solutions. The experimental results reported in Table 3 show clearly that COD and TOC removal are low. Indeed, with a specific energy about 4.5 GJ/m³, 27 and 26% of decrease are obtained, respectively, for COD and TOC whereas more than 97% of the initial NaPCP is removed. These results are in agreement with others studies investigated by Serpone et al. [2], Petrier et al. [22], Ku et al. [23] or Tiehm [24,25] with other aromatic compounds such as phenol and chlorophenol which also reveal a low mineralisation rate. The limiting step is the oxidation of organic intermediate products. So, the complete mineralisation would be possible only with a very extended irradiation time and so with a very high ultrasonic energy supplied.

3.1.3. Chemical pre-oxidative strategy

If ultrasonic oxidation appears to be an interesting way to degrade refractory and non-biodegradable organic compounds in aqueous solutions, time and energy scales to obtain a total mineralisation are still too large. Other chemical oxidation systems lead to the same conclusions (ozone [26–28], Fenton reagent [16], UV or photocatalysis [29,30], electron beam [31,32], etc.). Conversely, for bacteria, the limiting step is often the degradation of initial pollutants.

So, the chemical oxidation could be applied in order to enhance the biodegradability of the wastewater. The success of this strategy lies in adding judiciously the chemical oxidative agent in order to decrease the bacteriocidal effect of the toxic parent compound and to convert the resistant species into more easily metabolised oxidation products. Scott and Ollis [33] present an interesting synthesis of the studies realised on the integration of chemical and biological oxidation processes.

3.1.4. Toxicity

In order to evaluate the judicious dose of chemical oxidative agent that would be used before the biological treatment, the toxicity and the biodegradability of NaPCP solutions were measured after an ultrasonic oxidation. Toxicity measurement was undertaken previously by Gonze et al. [10]. Due to the very high toxicity of the NaPCP molecule, experiments were carried out with a low concentration (0.1 mM). Toxicity decreases rapidly to reach a minimum value for a specific energy supplied of 1.6 GJ/m³ as shown in Fig. 4. At this point, the samples are non-toxic. Then the toxicity increases sharply and remains stable at a high level (>80%). This unexpected behaviour can only be explained by the

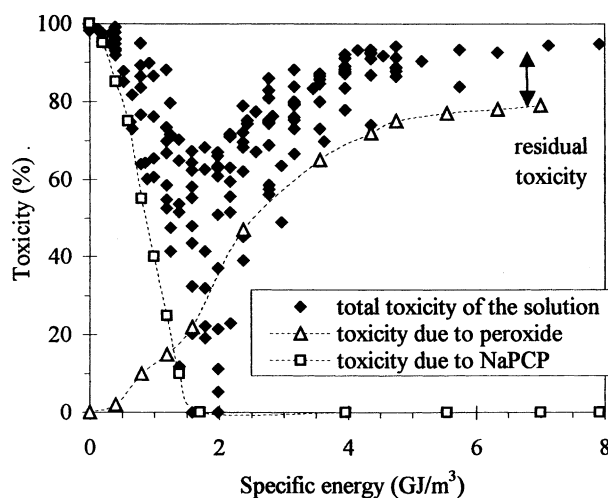


Fig. 4. Toxicities during the sonication of a 1 mM solution of NaPCP: total toxicity of the solution, toxicity due to hydrogen peroxide and toxicity due to NaPCP.

formation of toxic compounds especially hydrogen peroxide. It is confirmed by the distinction between the H_2O_2 toxicity and the total toxicity of the solution. Toxicity due to the NaPCP compound was calculated from its concentration measurement and the toxicity calibration curve (Fig. 2). In the same way, the toxicity of H_2O_2 is calculated. Then the total toxicity of the solution is the result of the decrease of the NaPCP concentration and the increase in toxic sonolysis products. Nevertheless, beyond 1.6 GJ/m^3 the total toxicity seemed to be higher than that obtained with H_2O_2 alone. This residual toxicity visualised by a double-headed arrow should indicate the presence of toxic organic compounds produced by the ultrasonic degradation of NaPCP. Even if we have shown that TCBQ and TCHQ are slightly toxic, we must suppose that there is the formation of other products which explain this residual toxicity.

3.1.5. Biodegradability

Biodegradability experiments were done with 1 mM pentachlorophenolate solutions and each experiment was duplicated in four runs. Table 3 summarises the BOD_5 inhibition as a function of the specific energy. The BOD_5 inhibition of the initial solution is $-48 \text{ mg O}_2/\text{l}$. To a 3.6 GJ/m^3 specific energy, it seems to be constant. So, the first intermediate by-products are not significantly less inhibiting than the parent compound. Nevertheless, we have shown that TCBQ and TCHQ are non-inhibitory so we can suppose the formation of other non-biodegradable products. For higher specific energies supplied (4.5 GJ/m^3), experiments display a negligible inhibition equal to $-7 \text{ mg O}_2/\text{l}$. So, the remaining parent compound and the oxidation products do not inhibit the biological activity. This biodegradability increase can be attributed either to the decrease of the parent compound to a less toxic concentration or the formation of more biodegradable intermediate products.

The sonication of water was undertaken in the same conditions. Results are also reported in Table 3. A BOD_5 reduction can be observed at the end of the treatment. For a specific energy of 4.5 GJ/m^3 , its value is about $-40 \text{ mg O}_2/\text{l}$. It is attributed to the hydrogen peroxide formation which, as described previously, interferes with the measurement due to the enzymatic catalase reaction. This interference can be lower with NaPCP solution because the hydroxyl radicals and hydrogen peroxide are probably partially scavenged by the organic compounds.

Tiehm [24,25] studied the biodegradation of synthetic solutions of 2,4-dichlorophenol (about 150 mg/l) and 2,3,5-trichlorophenol after ultrasonic treatment (360 kHz , 100 W , 500 ml). In both cases, ultrasonic pre-treatment led in the first time to the increase of toxicity on *V. fischeri* followed by a significant decrease. The biodegradability (BOD_{10}) is evaluated with addition of acetate or glucose. The results showed an increase of the BOD.

To conclude, the biodegradability evolution depends on several phenomena which interfere: the toxic parent compound concentration decreases; several toxic species are

perhaps formed; the metabolic value of the solution is decrease by its mineralisation. Nevertheless, the ultrasonic treatment is able to decrease the toxicity and to remove the inhibitory effect on biodegradation of NaPCP synthetic solutions. But, in order to evaluate the efficiency of this process, the oxidation of industrial wastewaters is then essential before using the ultrasonic process at the industrial scale.

3.2. Pre-oxidation of raw paper mill wastewaters

The three paper mill wastewaters described in the experimental part were sonicated in the same conditions than the synthetic solutions (500 kHz , 20°C , 60 W , between 400 and 650 ml). Only global measurements were undertaken (TOC, COD, toxicity, biodegradability, pH).

3.2.1. Concentrated basic wastewater (no. 1)

In spite of the high energy supplied (40 GJ/m^3), the sonication of this basic wastewater does not lead to a reduction in toxicity nor in COD. The initial toxicity was very high, more than 90% and did not show any decrease during experiment. The value of the pH did not change neither during the sonication. These results may be explained by the presence of high molecular weight compounds which were concentrated by ultrafiltration and are very difficult to oxidise. Ultrasound seems to be not an appropriate alternative for the treatment of this wastewater.

3.2.2. Basic wastewater (no. 2)

The sonication of the second basic wastewater less concentrated leads to an enhancement of the toxicity in the beginning of the treatment, which passes 90% with a specific energy of 80 GJ/m^3 (Fig. 5). It could be explained by the formation of organic products more toxic than the parent compound. After that, a significant decrease of toxicity and pH is observed whereas the COD and TOC decrease remains very weak until 100 GJ/m^3 (Fig. 6). At this time,

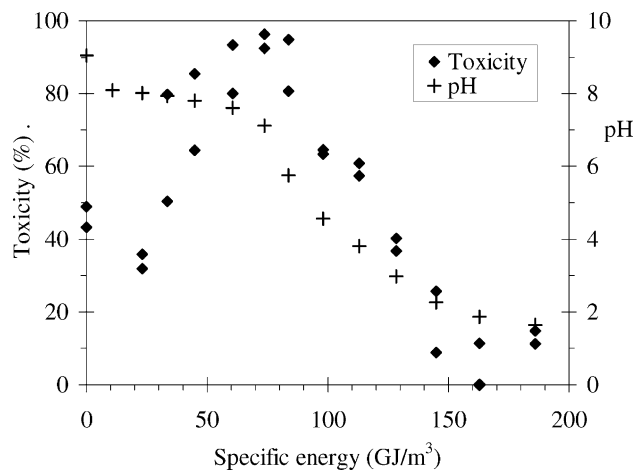


Fig. 5. Toxicity and pH vs. specific energy during sonication of the basic paper mill wastewater (no. 2).

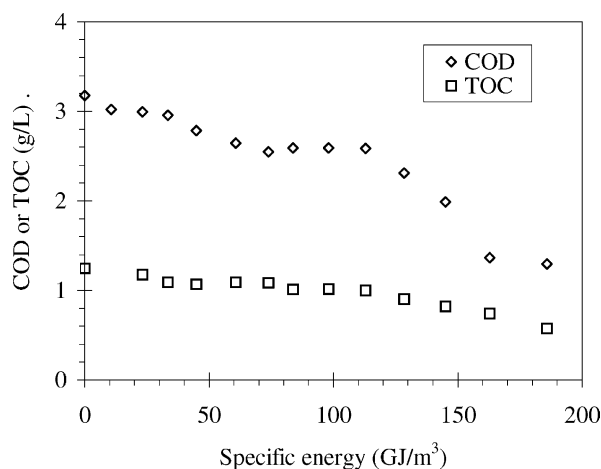


Fig. 6. COD and TOC vs. specific energy during sonication of the basic paper mill wastewater (no. 2).

the oxidation accelerates. The solution pH is about 5, value which corresponds to the transformation of bicarbonates in carbon dioxide [$pK_a(H_2CO_3/HCO_3^-) = 6.35$; $k(HCO_3^- + OH^\bullet) = 8.5 \times 10^6 \text{ l/mol s}$]. So when the solution is basic, radicals are trapped by bicarbonate ions due to their high concentration (205 mg/l). This fact has been observed previously by Cost et al. [34] with a nitrophenolic solution containing bicarbonates and by Beltran et al. [35,36] which treats with ozone a domestic wastewater with a high level of alkalinity. Another explanation is that the acidification of the solution leading to the protonation of the organic compounds makes their diffusion toward the bubble easier [23,37]. Then, the more hydrophobic protonated compounds are oxidised or pyrolysed more quickly. At the end of the sonication, the wastewater is considered as non-toxic and the abatement of the COD and TOC is about 60 and 54%.

The ozonation of paper mill wastewaters was studied by several authors [26,38,39] and did not lead to very positive results. Indeed, Freire et al. [26] observed a significant decrease of the phenolic compounds (90%), but a low removal of the COD (10%). Nevertheless, the inhibition factor measured with *E. coli* decreases from 60 to 40%. Sozanska and Sozanski [38] obtained around 40% on COD removal with the maximum dose of ozone (250 g/m³). Mao and Smith [39] obtained removals of 5 and 2%, respectively, for COD and COT with an ozone dose of 170 g/m³.

3.2.3. Acidic wastewater (no. 3)

The third wastewater contained low molecular weight compounds. At the end of the treatment a total decolouration was observed. pH, COD and TOC significantly decreased right from the beginning of the experiment (Figs. 7 and 8). There was no delay because there were no bicarbonates (4 mg IC/l) and the initial pH was about 6.

Oxidation and mineralisation is more than 80% with an energy supplied of 140 GJ/m³. As noted earlier, the presence of oxidisable mineral compounds as chlorides ions

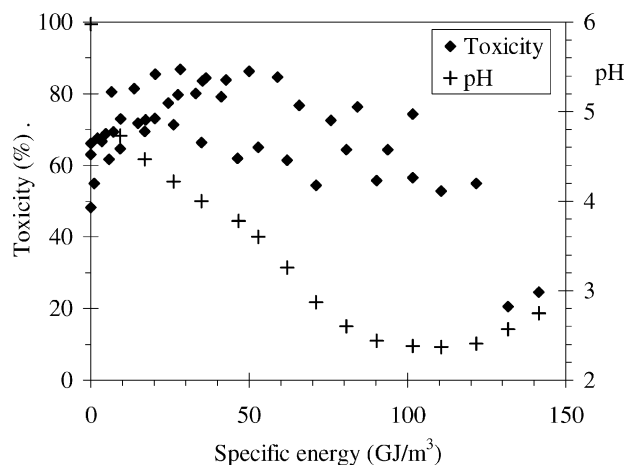


Fig. 7. Toxicity and pH vs. specific energy during sonication of the acidic paper mill bleach wastewater (no. 3).

can interfere with COD measures and increase its values. TOC is a more significant and realistic measurement which show that 84% of the organic matter was mineralised. The remained part should be in a high oxidised state. A pH decrease from 6 to 2 was observed to 100 GJ/m³, then a small increase was noted with a final pH value around 3. This phenomenon was also observed by Lin and Chuang [40] during the wet oxidation of a synthetic solution of phenol and was attributed to the oxidation of small organic acids formed during the treatment.

As with the basic wastewater no. 2, sonication of the acidic one leads to an enhancement of the toxicity in the beginning of the treatment (Fig. 7). The initial bioluminescence inhibition of 60% increases to 80% for a specific energy supplied of 50 GJ/m³. Then a large decrease can be noted and, at the end of the treatment, the wastewater is considered as non-toxic.

Concerning biodegradability, the dioxygen consumption during 5 days and the calculated value of BOD₅ are

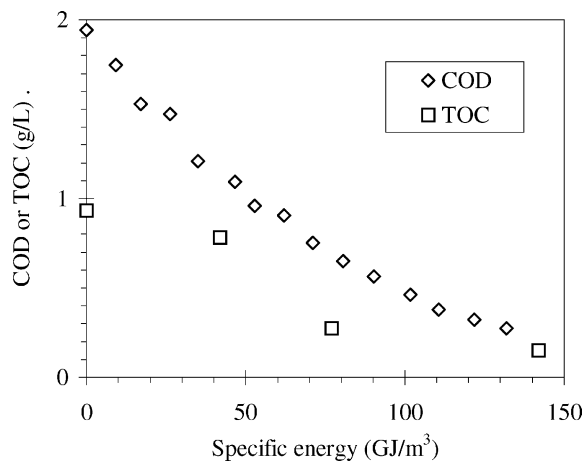


Fig. 8. COD and TOC vs. specific energy during sonication of the acidic paper mill bleach wastewater (no. 3).

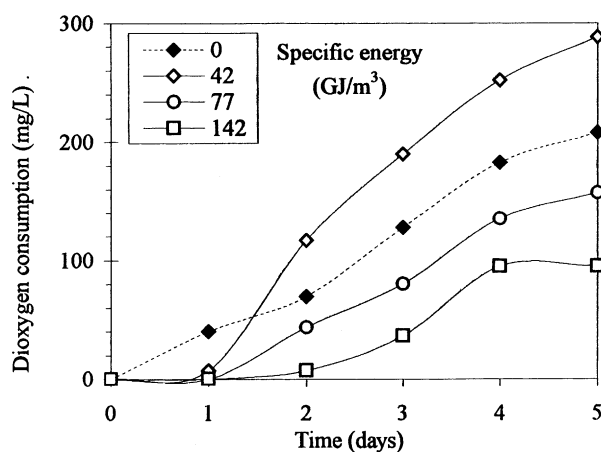


Fig. 9. Five days dioxigen consumption of the acidic paper mill wastewater (no. 3) before and after sonication (42, 77 and 142 GJ/m^3).

reported, respectively, in Fig. 9 and Table 4. The experiments reveal that, with these samples, the biodegradation was not finished after 5 days (Fig. 9). That means that a long bio-acclimation period is necessary and that the BOD_5 value minimise the biodegradable fraction. However, an increase of the BOD_5 can be noted in the beginning of sonication followed by a decrease. Thus, the biodegradability changes from 208 to 288 $\text{mg O}_2/\text{l}$, i.e. an increase of 38%. This preliminary increase can be attributed to the transformation of non-biodegradable species in more biodegradable forms. The decrease observed for a specific energy of 77 GJ/m^3 is the result of the global oxidation which leads to an abatement of biologically oxidisable matters and means that the treatment may be stopped at this point. These conclusions are confirmed by the calculation of a significant representation of the biodegradability which is given by the ratio of BOD_5 to COD. This ratio increases at the beginning of the treatment and remain stable for a specific energy upper than 42 GJ/m^3 . Generally, a BOD_5/COD ratio higher than 0.4 is considered as an indication of an easy biodegradability of the sample. In these experiments, this value initially equal to 0.11 reaches 0.29 at the end of the treatment which indicates an increase of the biodegradability.

Wang et al. [31] irradiated an acidic paper mill bleach wastewater by an electron beam. An increase of BOD_5/COD ratio from 0.07 to 0.2 with a radiation dose of 800 krad was observed (COD fall of 13.5%, BOD increase of 58.6%). Any

Table 4
COD, TOC, BOD_5 and BOD_5/COD vs. specific energy during sonication of the acidic paper mill wastewater no. 3

Specific energy (GJ/m^3)	TOC (mg C/l)	COD ($\text{mg O}_2/\text{l}$)	BOD_5 ($\text{mg O}_2/\text{l}$)	BOD_5/COD
0	934	1943	208	0.11
42	782	1141	288	0.25
77	273	691	157	0.23
142	151	323	95	0.29

subsequent BOD_5 decrease was noted. It should be noted that their initial sample is more toxic and less degradable than our effluent. Berge et al. [32] also irradiated a paper mill wastewater by an electron beam with two adsorbed doses (10 and 50 kJ/kg). The biodegradability (BOD_{28}) remained constant with 10 kJ/kg and was depressed with 50 kJ/kg . If a peroxide treatment is applied before the radiolysis, the biodegradability is enhanced.

3.3. Post-oxidation of a treated landfill leachate

In the case of biodegradable wastewaters with small amounts of recalcitrant compounds, the chemical oxidation should follow a biological treatment because this last one is generally less expensive than the first one. For example, Haberl et al. [41] showed that, with a pulp bleaching wastewater which contains 50% of biodegradable species, an initial biological treatment is a preferable strategy that an initial chemical oxidation. In one of their systems, Heinze et al. [27] studied pulp and paper bleach wastewaters which periodically moved from the ozonation to the biological steps (fluidised-bed reactor inoculated with aerobic acclimated biological seed). Nevertheless, it was not possible to highlight a significant synergistic effect between the two treatments.

The last part of this study is devoted to the assessment of the ultrasonic process efficiency as a post-treatment trough the oxidation of a biologically pre-treated landfill leachate. Experiments were carried out in the same conditions than the paper mill wastewaters. The sonication leads to an increase of the toxicity from 0, at the beginning of the treatment, to 90% at 20 GJ/m^3 which shows the formation of toxic intermediates products (Fig. 10). At the same time, no increase of the BOD_5 is observed and only a very few amount of COD and TOC is removed (Fig. 11, Table 5). As with wastewater no. 2, the detrimental effect of bicarbonate ions is obvious. Around 35 GJ/m^3 , the pH decreases promptly from 7 to less than 3 due to the formation of organic acids.

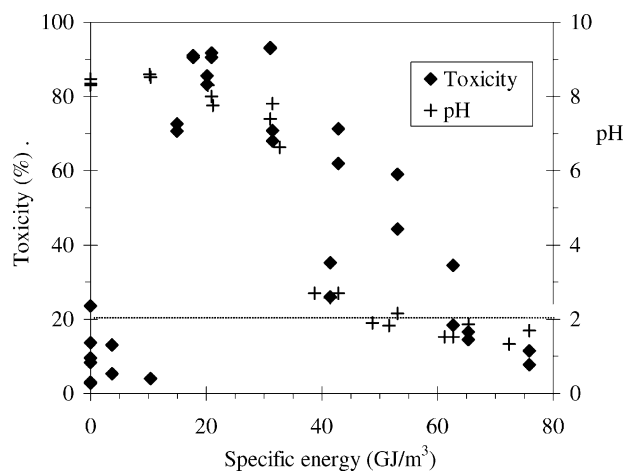


Fig. 10. Toxicity and pH vs. specific energy during sonication of the landfill leachate.

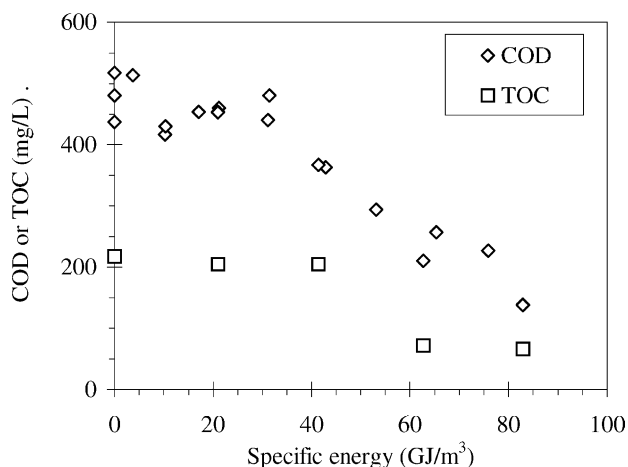


Fig. 11. COD and TOC vs. specific energy during sonication of the landfill leachate.

This acidification removes bicarbonate ions and leads to the protonation of pollutants promoting their entrance in the bubbles. Then, TOC shows a significant decrease and the removal reaches 70% at the end of the treatment (80 GJ/m³). This mineralisation is correlated to a decrease of the toxicity. Indeed, if the treatment is carrying on, the toxicity decreases to its initial non-toxic value. The BOD₅ shows an increase from 0 to 29 mg O₂/l at 63 GJ/m³; then, BOD₅/COD ratio reaches 0.14. This value remains low. The increase of BOD₅ due to the formation of biodegradable compounds is minimised by its simultaneous decrease due to the mineralisation of 70% of the COT present in the leachate.

Other authors studied the post-chemical oxidation of landfill leachates. Imai et al. [42] investigated the ozonation of a treated leachate from an old landfill which have similar properties than our wastewater. During the first 60 min of ozonation, a slight COD decrease (24%) and an increase of the BOD₅ from 5 to 44 mg O₂/l were noted. At the end of the treatment (420 min and 900 g O₃/m³), the BOD₅ returned to its initial value and 72% of the COD was removed. So, the BOD₅/COD ratio initially equal to 0.03 reached 0.12. Ince [43] investigated the oxidation of a pre-treated leachate by a combination of ozone, UV and hydrogen peroxide. This treatment led to a decrease of COD and TOC of 83 and 69%, respectively. Papadopoulos and co-workers [44–46] looked for the best combination of biological and chemical

Table 5
COD, TOC, BOD₅ and BOD₅/COD vs. specific energy during sonication of the landfill leachate

Specific energy (GJ/m ³)	TOC (mg C/l)	COD (mg O ₂ /l)	BOD ₅ (mg O ₂ /l)	BOD ₅ /COD
0	217	458	0	0
21	205	453	0	0
41	205	367	18	0.05
63	72	210	29	0.14
83	66	138	15	0.11

treatments for leachates from an old landfill. Their study showed that the more effective combination is a first biological oxidation followed by the chemical one and finished with a second biological stage. Indeed, the first biological treatment removed the biodegradable fraction containing in the wastewater, the chemical one oxidised refractory species in biodegradable compounds and the last biological stage eliminated the remaining COD and BOD₅ fractions. This process removed 99% of the BOD₅ and 73–83% of the COD with two stages of 7 days in acclimated sludge and 24 h in contact with H₂O₂ and FeSO₄.

4. Discussion

Efficiency of chemical pre- or post-oxidation strategy is determined by the nature and the concentration of the wastewater and the amount of the oxidative agent supplied.

4.1. Nature of the wastewater

The ultrasonic process, as other advanced oxidation processes, involves the formation of HO• as oxidative radicals, which are very reactive but non-selective oxidants. For NaPCP solutions, this oxidative reagent indiscriminately oxidises the initial pollutant and the intermediate compounds formed. Toxic pollutants can be degraded but also all the other compounds present in the solution even if they are non-toxic and biodegradable. In the case of a real wastewater, this difficulty is amplified by the complexity of the wastewater composition.

The ultrasonic oxidation presents a particularity due to the presence of cavitation bubbles (biphasic reaction) and due to the second reaction pathway (pyrolysis). The compound properties seem to dictate the reaction way and rate. Usually, it is postulated that hydrophobic and volatile compounds are pyrolysed in the cavitation bubble, whereas the hydrophilic and poorly volatile ones are oxidised in the hot liquid surrounding the bubble and/or in the bulk of the solution [39,47]. These last reactions need the presence of radicals which are formed in the bubble and diffuse in the solution during the collapse. But in the case of a mixture of pollutants, a lot of radicals can be scavenged by the hydrophobic compounds. So, only a few of them can escape from the bubble and react with hydrophilic compounds in the solution before to recombine. This “selectivity” can be unfavourable to the destruction of toxic compounds. Another problem is the accumulation of species inside the bubbles that decreases the temperature reached in the collapsing bubble by depressing the specific heat ratio. These observations can explain that a very high energy is necessary to obtain an important oxidation of our wastewaters.

4.2. Amount of the pre-oxidative agent

The major difficulty, linking to the non-selectivity of the chemical oxidative processes, is that the amount of the

oxidative agent depends on the nature and the concentration of the wastewater. In all cases, the optimal efficiency of the overall process is found when the dose of the chemical oxidative agent is (i) sufficient to eliminate the possible toxic and non-biodegradable intermediates formed, (ii) not too high in order to prevent a consequent decrease of the wastewater metabolic value.

The synthesis of intermediate compounds more toxic and less biodegradable than the initial compound was referred by several authors. But generally they precise that if the quantity of the oxidative agent is enhanced, these intermediate products are oxidised and the biodegradability is increased. Manilal et al. [29] investigated the photocatalysis of a pentachlorophenol solution and observed an increase of the bioactivity inhibition due to the presence of toxic intermediate compounds. Nevertheless, if the oxidation is carried out longer, this inhibitory character can be totally removed even if the solution remains non-biodegradable. Gilbert [48] reported that the ozonation of biodegradable aromatic compounds as aniline and aminobenzoic acid can lead to the formation of primary intermediates difficult to degrade biologically. Bowers et al. [15] found an increase and subsequently decrease of the toxicity with 2,4-dichlorophenol submitted to Fenton's reagent. Beltran et al. [35,36] oxidised a domestic wastewater by ozonation combined with a biological treatment. He studied the amount of ozone used and the results obtained on biodegradability. He observed that a large ozone dose could lead to a decrease of the BOD because of the oxidation of biodegradable compounds. So, it results in the decrease of the biological treatment efficiency and the increase of the treatment cost. Scott and Ollis [33] noted that an overdose of the chemical oxidation may result in highly oxidised products with a little metabolic value for the micro-organisms and in an excessive cost. Takahashi et al. [49] investigated the ozonation of phenol and showed that the biodegradability (through the BOD₅/TOC ratio) increased. They concluded that the first products are more biodegradable than the parent compound. With non-biodegradable compounds as *o*-, *p*-, 2,4-, 2,6-, 2,4,6-nitrophenol, they observed an important increase of the biodegradability then a decrease that is attributed to the formation of low biodegradable products. Loizidou et al. [44] studied the oxidation of a landfill leachate by the Fenton process. The author demonstrated that the optimal experimental conditions are 100 ml H₂O₂/l and 40 g FeSO₄/l. If the amount of the oxidant is doubled, the performances of the process in term of COD removal are not significantly improved.

These examples show that it is essential to evaluate the optimal dose of the chemical oxidative agent, to decrease the toxicity and increase the biodegradability sufficiently to achieve the treatment with a conventional biological step. Karrer et al. [50] propose a test to evaluate the applicability of a combined treatment and to determine the optimal dose of each process.

5. Conclusion

In the case of the concentrated basic paper mill wastewater, the treatment is inefficient in spite of the high energy supplied. This can be due to the properties of this wastewater that contains a lot of high molecular weight compounds which are refractory to ultrasound. With the second less concentrated wastewater and the leachate, a significant delay appears which can be explained by the presence of species such as carbonates ions that can trap free radicals and so decrease the efficiency of the oxidation. In these cases, the acidification of the solution leading to the protonation of compounds may account for the acceleration of oxidation and mineralisation. At the end of the treatment, these wastewaters are non-toxic and their biodegradability is improved. The ultrasonic irradiation of the acidic paper mill wastewater leads to positive results on toxicity, oxidation, mineralisation rate and biodegradability.

So we can conclude that the ultrasonic process combined with a biological treatment as a pre- or a post-treatment can be considered as an interesting option for the depollution of toxic and poorly biodegradable wastewaters. The amount of energy supplied and the position of the chemical treatment depends on the nature of the wastewater treated and must be investigated in order to minimise the energy cost.

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