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Chemical Engineering Journal 73 (1999) 93–100

Chemical Engineering Journal

Wastewater pretreatment with ultrasonic irradiation to reduce toxicity

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Received 28 January 1998; received in revised form 7 September 1998; accepted 18 December 1998

Abstract

In order to industrialize an ultrasonic process for wastewater treatment, several works were undertaken. The first one was the study of pentachlorophenol degradation [E. Gonze, Y. Gonthier, P. Boldo and A. Bernis, Can. J. Chem. Eng. 75 (1997) 245]. Association of high-frequency ultrasound transducers was investigated [E. Gonze, Y. Gonthier, P. Boldo and A. Bernis, Entropie 204 (1997) 21] and the mapping of ultrasonic fields in various reactors was studied [E. Gonze, Y. Gonthier, P. Boldo and A. Bernis, Chem. Eng. Sci. 53 (1998) 523; V. Renaudin, N. Gondrexon, P. Boldo, C. Pétrier, A. Bernis and Y. Gonthier, Ultrasonics Sonochem. 1 (1994) S81]. The third step presented here consists of considering the ultrasonic process as a preoxidation treatment before a classical biological purification. During the ultrasonic irradiation of a sodium pentachlorophenate solution (NaPCP), the concentration of NaPCP, the acute toxicity effects on bacteria (*Vibrio fischeri*) and on daphnids (*Daphnia magna*) as well as the biodegradability of the pollutant solution were simultaneously monitored. Experimental results provide evidence that an ultrasonic treatment is an efficient preoxidation step.

Keywords: Ultrasound; Wastewater treatment; Pentachlorophenol; Toxicity; Biodegradability

1. Introduction

In the 1960s, the development of sonochemistry revealed a new and very promising application: the treatment of industrial and domestic wastewater with ultrasonic energy. Indeed, the growing need to eliminate hazardous pollutants from sewage brought several researchers to take an active interest in the reactivity under ultrasonic irradiation. These first studies [1,2] exhibited thereby the feasibility of the process.

1.1. Ultrasonic reactivity

Mechanisms involved in sonochemical transformations are still misidentified. However, acoustic cavitation appeared early as the main phenomenon responsible for chemical transformations [3,4]. Several modes of reactivity have been proposed: pyrolytic decomposition, hydroxyl radical oxidation, plasma chemistry and supercritical water oxidation.

The first one, i.e., pyrolytic decomposition, takes place inside the cavities and affects the vapour from the liquid medium or dissolved organic compounds which may penetrate into the bubbles. Indeed, energy concentrated in the bubbles is sufficient to break strong chemical bonds. In aqueous solutions, the main pyrolytic reaction is the dissociation of water. This thermal dissociation leads to the production of highly reactive radicals ($OH^{\bullet}$, $H^{\bullet}$) inside the bubbles [5]. These radicals may recombine inside or around the bubbles according to the reactions brought about together by Wu, Huang and Livengood [6]. Nevertheless, if these radicals, after their migration to the bulk solution, are likely to be in contact with some dissolved molecules, they will be able to oxidize the latter. It seems that the ratio between hydroxyl radical oxidation and pyrolysis depends on the localization of the solute (in the bulk solution, inside the bubble or in the interfacial layer) and therefore, on its physico–chemical properties (Table 1). But there are still many unknown parameters to be found. Henglein [7] pointed out that the main property determining the entrance of a compound into the bubble was its hydrophobicity rather than its vapour pressure. Thus hydrophilous organic compounds like phenol and chlorophenols may undergo a hydroxyl radical attack in the bulk solution or in the interfacial film. Some other more hydrophobic compounds like carbon tetrachloride, benzene and chlorobenzenes may be mainly pyrolyzed inside the bubble. However, some other cases remain for which the localization of degradation is less easy or for which there seems to be a competition between mechanisms. So is the case with *p*-nitrophenol and some

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1385-8947/99/$ – see front matter
PII: S1385-8947(99)00021-2

Table 1
Degradation of air-equilibrated solutions of different compounds

Compounds	References[a]	Conditions of sonication	Intermediate products identified[b]	Major mechanism[c]
Phenols				
Phenol	[28][d]	20 and 487 kHz, 30 W, air, 0.5 mM	hydroquinone[d], catechol,[d] *p*- and *o*-benzoquinone[d] 2,5-dioxohexen-3-dioic acid, muconic, maleic, succinic, formic, propanoic, oxalic and acetic acids	R
	[29]	20 and 541 kHz, 30 W, air, 100 mg/l		
2-chlorophenol			chlorohydroquinone, catechol, 3-chlorocatechol, chlorides	R
3-chlorophenol	[30]	20 kHz, 50 W, air, 0.05 mM	chlorohydroquinone, 3- and 4- chlorocatechol, chlorides	R
4-chlorophenol			hydroquinone, 4-chlororesorcinol, 4-chlorocatechol, chlorides	R
2,4-dichlorophenol	[20]	B.F., Ar	2-chlorophenol, 4-chlorophenol, 2,4-dichlorocatechol, chlorohydroquinone, 2,4-dichloresorcinol, 2,6-dichlorohydroquinone, chlorides	R
Pentachlorophenol	[23]	500 kHz, air, 0.1 mM	chlorides	R
Parathion	[31]	20 kHz, 84 Welec, air	*p*-nitrophenol, sulfates, phosphates	P
p-nitrophenol	[32]	0.1 mM	nitrites, nitrates, formic, oxalic and acetic acids, 4-nitrocatechol, benzoquinone, hydroquinone	R + P
Benzenes				
Benzene	[33][d]	20 and 487 kHz, 30 W, air, 0.5 mM	phenol[d], catechol[d], hydroquinone[d], *p*- and *o*-benzoquinone[d], 1,2,3-trihydroxybenzene, maleic and muconic acids, formaldehyde, acetylene[d]	P + R
	[1]	800 kHz, 1.5 kW, air, 2.56 mM		
Chlorobenzene	[33]	20 and 487 kHz, 30 W, air, Ar, O_2, 0.5 mM	4-chlorophenol, 4-chlorocatechol, hydroquinone, acetylene	P + R
Chlorinated aliphatic hydrocarbons				
Carbon tetrachloride	[24]	20 and 500 kHz, 30 W, air, 0.035 mM	main intermediates: tetrachloroethylene[d], hexachloroethane[d]	
	[34][d]	20 kHz, 135 W, Ar, 0.0195–0.195	small amount of: dichlorocarbene[d], dichloromethane, trichloroethylene, tetrachloroethane, pentachloroethane, hexachloropropene, hexachlorobutadiene, chloroform final products: chlorine, chlorides[d], chlorhydric acid, hypochlorous acid[d]	P
Chloroform	[35]	200 kHz, O_2, Ar, air		P
	[19]	20 kHz, 200 W, air		P
Methylene chloride	[19]			P
1,2-dichloroethane	[19]			P + R?
1,1,1-trichloroethane	[35]			P + R?
Trichloroethylene	[19,35]		chlorides, hydrogen, chlorhydric acid, (methane, ethylene)	P + R?
Tetrachloroethylene	[19,35]			P + R?
Mixtures				
Carbon tetrachloride + phenol	[17]	20 and 500 kHz, 30 W, air, phenol: 0.5 mM, CCl_4: 3.8 mM	chlorides, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, *p*- and *o*-benzoquinone, chlorobenzoquinone, 2,6-dichlorobenzoquinone	

[a] Main works only.
[b] In aqueous or gaseous phase.
[c] Responsible for the first degradation step (R: radical attack, P: pyrolysis).
[d] The author detected only these products.

hydrocarbons. In conclusion, hydrophobic and volatile organic compounds are destroyed very easily, whereas non-volatile and hydrophilous compounds are more difficult to oxidize by ultrasound. To improve the reactivity of these compounds is an important challenge.

The third mode of reactivity proposed is that of plasma chemistry. Lepoint and Mullie [8,9] observed some similarities between coronaluminescence and sonoluminescence as well as between coronachemistry and sonochemistry. This led them to assimilate the ultrasonic effects to corona effect discharges and to suggest the formation of microplasmas inside the bubbles.

The above-mentioned hypothesis attributes the sonochemical reactions to supercritical water. Indeed, Hoffmann [10,11] proposed the existence of a layer in the bubble-solution interface where temperature and pressure may be beyond the critical conditions (647 K, 22.1 MPa) and which may have physical properties intermediate between those of a gas and a liquid. These conditions may improve the reactivity by modifying, in particular, the solubility and the diffusion of the solutes. This interface of supercritical water may have a lifetime and a spatial extent to the order of milliseconds and micrometers, respectively. However, this hypothesis for supercritical water is still much debated.

1.2. Ultrasonic wastewater treatment

For the past 10 years, some systematic studies have aimed at analyzing the reactivity of organic compounds. The results of the same as well as our own results [12–16] seem to demonstrate that total mineralization of pollutants is difficult to obtain with ultrasound alone, in particular, with mixtures of pollutants [17–21]. All the authors report that the final products of degradation are short-chain organic acids, carbon dioxide and inorganic ions. But the time-scale and the dissipated power necessary to obtain the complete mineralization of hazardous pollutants are not economically acceptable. So the ultrasound process is studied in this work as a preoxidation step before a biological treatment which will carry on mineralization as far as possible.

Concerning the influence of frequency, it appeared very early [2] that phenol oxidation, very slow at low frequency (25 and 55 kHz), becomes fast at high frequency (800 kHz) at the same input power. The better efficiency achieved at high frequencies was confirmed by Pétrier for the oxidation of iodide ion [22], sodium pentachloro-phenate [23] and carbon tetrachloride [24] as well as for hydrogen peroxide formation [25]. Therefore, in our study, a high-frequency technology (500 kHz) was chosen.

2. Experimental

2.1. Materials and reagents

The experimental set-up used was composed of an electrical generator (frequency 500 kHz, power 0–100 W) supplying a transducer fixed on a reactor module (Fig. 1). The transducer consisted of a piezoelectric ceramic (diameter 40 mm) stuck under a stainless steel plate (diameter 80 mm). The reactor module (capacity 1 l) was built with a glass jacket which allowed the circulation of the cooling fluid. A sampling loop allowed to follow the pollutant degradation.

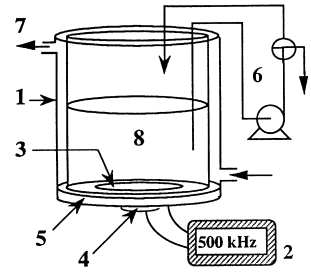

Fig. 1. Experimental set-up. (1) glass jacket: internal diameter = 100 mm; (2) high-frequency (500 kHz) generator; (3) stainless steel plate; (4) piezoelectric ceramic; (5) PVC bottom plate; (6) sampling loop; (7) cooling fluid and (8) solution to treat.

Sodium pentachlorophenate was chosen as a model compound. It has been investigated previously by Pétrier [23] and Gondrexon [13]. For all experiments, the initial concentration of sodium pentachlorophenate was 0.1 mM. The pollutant was dissolved in a basic solution (pH = 12) obtained by adding sodium hydroxide. The pH was then adjusted with phosphoric acid to fall within a 6.8–7.5 range. The irradiated solution volume was either 250 or 500 ml. The dissipated power, evaluated by a calorimetric measurement, ranged from 55–65 W and the temperature was maintained at $20 \pm 2^{\circ}C$.

The pentachlorophenate concentration was monitored using a high performance liquid chromatograph as described in our previous paper [12]. Hydrogen peroxide concentration was measured with analytical test strips (MERCK).

2.2. Toxicity measurements

Two toxicological tests were chosen from among the great number of existent normalized tests to measure the acute toxicity of organic compounds. The first test evaluated the bioluminescence inhibition in bacteria exposed to the pollutant, while the second evaluated the mobility inhibition in daphnids.

2.2.1. Toxicity effects on marine bacteria (Vibrio fischeri)

This normalized test (norm AFNOR T 90–320) is based on the measure of bioluminescence from the marine bacteria *V. fischeri*. The main property of these bacteria is their capacity to emit light. The luminous intensity is proportional to the quantity of living bacteria. This intensity is the number of photons emitted during 10 s and is measured with a luminometer (PRODEMAT Lucy).

During ultrasonic treatment of the NaPCP solution, samples (200 μl) were taken at different sonication times.

Aliquots of bacteria suspension (200 μl) containing bacteria culture, nutritive compounds and sodium chloride were added to each sample. The bacteria were mixed with the sample during the exposure period (t). The luminous intensity emitted by each suspension was measured before (I_{0e}) and after (I_{te}) this exposure. The sample toxicity was calculated as follows (BR represents the emission from a control tube containing only bacteria suspension without pollutant):

$$\Delta\% = \frac{(I_{0e}\mathrm{BR}) - I_{te}}{I_{0e}\mathrm{BR}} \times 100 \quad (1)$$

$$\mathrm{BR} = \frac{I_{tb}}{I_{0b}} \quad (2)$$

According to the norm, every sample wherein the inhibition is less than 20% can be considered non-toxic. Since *V. fischeri* are sensitive to medium acidity, the norm imposed the maintenance of pH between 5.5 and 8.5. But then the ultrasonic irradiation of an aqueous solution resulted in a pH decrease owing to the formation of protons and the oxidation of dissolved nitrogen into nitrites and nitrates. Hence for long irradiations, sample acidity was neutralized by adding sodium hydroxide.

2.2.2. Toxicity effects on daphnids (Daphnia magna)

The ecotoxicological test employed here (norm AFNOR T 90–301, equivalent to ISO 6341) determines the 'concentration' of toxic solutions resulting in the immobilization of 50% of the waterflea *D. magna* after a 24 h exposure. The 'concentration', expressed in percent, is called 24 h-IC50 and the toxicity is proportional to inverse IC50. Each sample taken during sonication was diluted at five different dilutions: five aliquots of the sample (between 0.5–10 ml) were placed in five test-tubes that were then filled up to 10 ml with a specific mineral medium. Five daphnids (less than one-day old) were then placed into each test tube. These tubes were covered with plastic stoppers to avoid evaporation and kept in the dark at 20 ± 1°C without aeration. After a 24 h exposure, the daphnids that were unable to swim were considered as immobilized. Percentages of immobilization were calculated and plotted as a function of concentration on log–probit paper. IC50 was directly read as the abscissa of the point corresponding to 50% immobilization.

2.3. Biodegradability

Biodegradability is a complementary parameter for evaluating the possibility of using biological treatment. This test finds out if the ultrasonic irradiation of a NaPCP solution makes it possible to degrade the effluent by microorganisms from a sewage treatment plant.

Owing to the bulky equipment often involved in this kind of tests, a protocol was defined, adapted from several norms regarding the evaluation of the aerobic biodegradability of organic compounds. A mineral medium was the one recommended by the international norms ISO 7827, 9888 and 9439. A stock solution was prepared by dissolving the following salts in 1 l deionised water: 0.283 g KH_2PO_4; 0.7243 g K_2HPO_4; 0.8871 g Na_2HPO_4 and 0.0333 g NH_4Cl. Samples of pentachlorophenate solution were taken at different sonication times. 70 ml of the sample were added to 30 ml of mineral medium in vessels. Each vessel was inoculated with 30 mg l^{-1} of activated sludge taken from the aeration basin in the domestic and industrial sewage treatment plant of Bourgoin–Jallieu (France). This sludge was chosen because the above-mentioned treatment plant is well-adapted to industrial wastes. Each vessel was aerated and mixed with a magnetic stirrer. The biodegradability of the irradiated NaPCP solutions was followed for 28 days by the measurement of toxicity by the bioluminescence test described above. Measures allowing observing the persistence of toxic compounds in the solution were undertaken. Indeed, if toxicity decreased during the 28-day test, it means that the microorganisms were able to degrade the toxic compound. However, this test does not point out the evolution of non-toxic compounds. It would, therefore, be necessary to complete this test with a measure of TOC or BOD.

3. Results and discussion

3.1. Kinetic of pentachlorophenate ultrasonic degradation

In our experimental conditions, pollutant degradation followed an apparent first-order kinetic [12]:

$$[\mathrm{NaPCP}] = [\mathrm{NaPCP}]_0 \exp\left(-k_{\mathrm{th}} \frac{P_{\mathrm{th}}}{V} t\right) \quad (3)$$

The disappearance rate is proportional to the power density applied, and the kinetic pseudo first-order rate constant, k_{th} ($m^3\,J^{-1}$), is representative of ultrasonic efficiency. Fig. 2 which reports the evolution for a

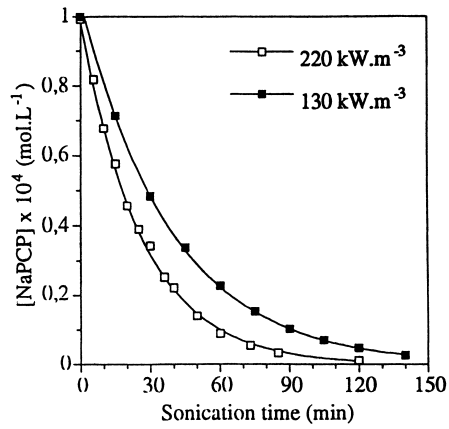

Fig. 2. Kinetic of pentachlorophenate ultrasonic degradation with two power densities (points: experimental results; lines: kinetic model results). The degradation rate is proportional to the power density dissipated in the solution.

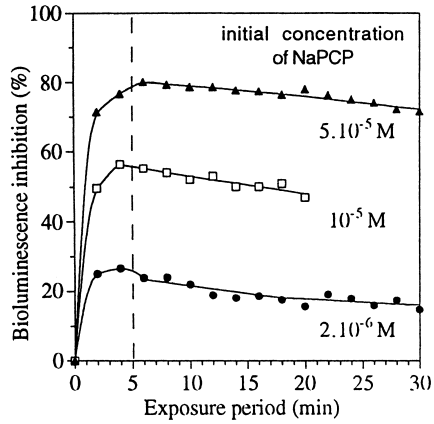

Fig. 3. Measurement of toxicity effects on marine bacteria : choice of exposure period as regards the sample and the bacteria. A greater response is obtained for 5 min, after which bioluminescence inhibition decreases very slowly.

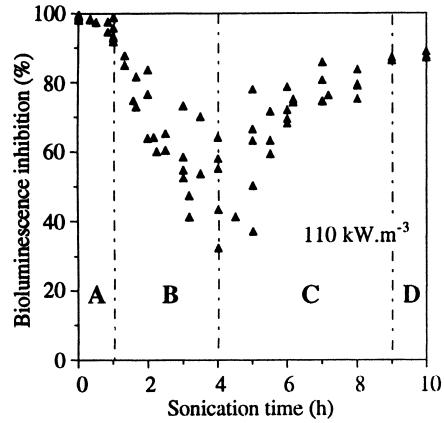

Fig. 5. Measurement of toxicity effects on marine bacteria : bioluminescence inhibition versus period of sonication (at a power density of 110 kW m^{-3}). The smaller toxicity of the solution is obtained after about 4 h of sonication.

NaPCP concentration for two different power densities (130 and 220 kW m^{-3}), provides validation of the kinetic model.

3.2. Evolution of toxicity

3.2.1. Toxicity effects on marine bacteria

Preliminary experiments consisted of choosing the exposure period and plotting calibration curves. Several exposure periods between 2–30 min were tested (Fig. 3). For the following experiments, the exposure period was 5 min because the response amplitude (inhibition percentage) was then large and seemed to become almost constant. The calibration curves (Fig. 4) indicate the inhibition percentage as a function of the concentrations of NaPCP (10^{-7}–10^{-4} M) and H_2O_2 (10^{-5}–10^{-2} M). These curves show that the solution in which the concentration is less than about 10^{-6} and 3×10^{-4} M for pentachlorophenate and hydrogen peroxide, respectively, can be considered as non-toxic. The optimal utilization field ranges between 20–80% of inhibition. Beyond 80%, the test saturates, hence the samples must be diluted.

The evolution of toxicity for a pentachlorophenate solution during ultrasonic irradiation was then evaluated. Figs. 5 and 6 represent the inhibition percentage as a function of the sonication time for power densities 110 and 220 kW m^{-3}, respectively. The shape of these curves is similar but the dispersion of the results remains important for low toxicity (<40%). Four zones can be differentiated. In zone A, toxicity is very high (>95%). The decrease is not significant because the test saturates. However, measurements carried out after diluting the samples 10 times with a sodium chloride solution allowed the visualization of the decrease in toxicity (Fig. 7). In zone B, toxicity decreases fast and reaches a minimum value of about 30%, which is above the toxicity limit fixed by the norm. In initial concentration

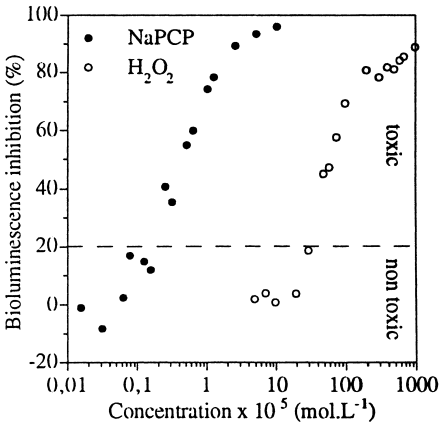

Fig. 4. Measurement of toxicity effects on marine bacteria : calibration curves of bioluminescence as a function of pentachlorophenate and hydrogen peroxide concentrations. Bioluminescence inhibition increases with pollutant concentration.

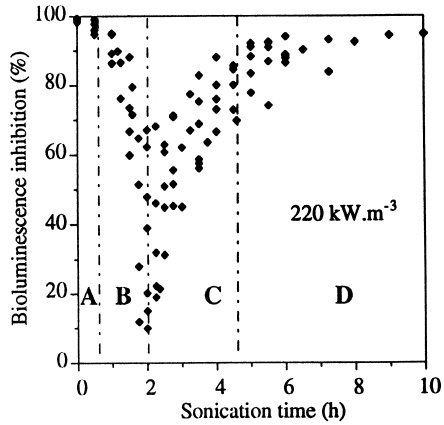

Fig. 6. Measurement of toxicity effects on marine bacteria: bioluminescence inhibition vs. period of sonication (at a power density of 220 kW m^{-3}). The smaller toxicity of the solution is obtained after about 2 h of sonication.

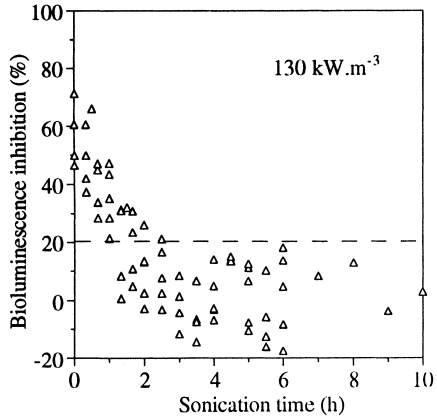

Fig. 7. Measurement of toxicity effects on marine bacteria : bioluminescence inhibition in the samples diluted 10 times versus the period of sonication (at a power density of 130 kW m^{-3}).

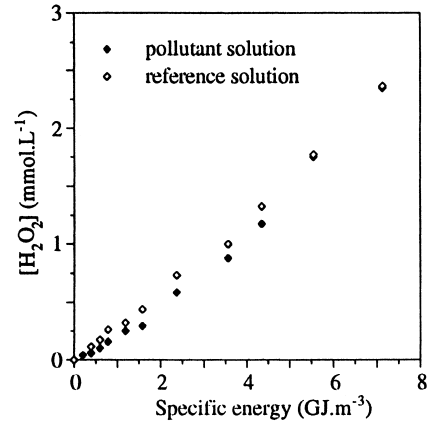

Fig. 9. Production of hydrogen peroxide in reference and pentachlorophenate solutions versus dissipated ultrasonic specific energy.

conditions, this minimum is reached after a 2 h and 4 h sonication when the power density is 220 and 110 kW m^{-3}, respectively. This corresponds, in both cases, to a specific energy of 1.6 GJ m^{-3}. In zone C, toxicity increases sharply again and then remains stable in zone D at a high level (>80%). The synthesis of toxic compounds only during sonication may explain this increase in toxicity.

In order to identify the causes behind this increase in toxicity in zones C and D, several experiments were carried out. First, the toxicity of a 'reference solution' was compared to that of a NaPCP solution during sonication. The reference solution was water containing the same concentrations of sodium hydroxide and phosphoric acid as the NaPCP solution. As shown in Fig. 8, the sonicated reference solution rapidly became as toxic as the NaPCP solution. So the increase in toxicity is essentially due to some products of water sonolysis and not those of NaPCP ultrasonic degradation. In fact, this toxicity has been attributed to hydrogen peroxide. Several ways of forming hydrogen peroxide have been proposed [26]. The main one seems to be the recombination of hydroxyl radicals Eq. (5) and, in a smaller proportion, the reaction between hydrogen and hydroperoxyl radicals Eq. (7):

$$H_2O \rightarrow OH^{\bullet} + H^{\bullet} \quad (4)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (5)$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad (6)$$

$$HO_2^{\bullet} + H^{\bullet} \rightarrow H_2O_2 \quad (7)$$

Further experiments consisting of the measurement of hydrogen peroxide were undertaken (Fig. 9). Hydrogen peroxide concentration is reported as a function of the specific energy dissipated during sonication of the reference solution and the NaPCP solution. The results point out that the increase in H_2O_2 is similar in both solutions, and consequently, that H_2O_2 results from water sonication only.

Fig. 10 confirms the importance of hydrogen peroxide, the toxicity due to the NaPCP compound being differentiated from that due to hydrogen peroxide. These two different toxicities are reported as a function of the dis-

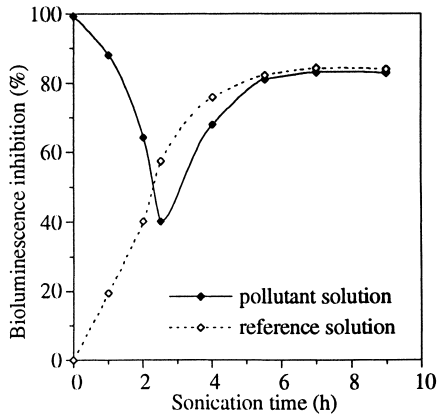

Fig. 8. Measurement of toxicity effects on marine bacteria : comparison of the toxicity of both reference and pentachlorophenate solutions. The increase in toxicity after about 2 h seems to be essentially due to a product of water sonolysis and not one of NaPCP sonolysis.

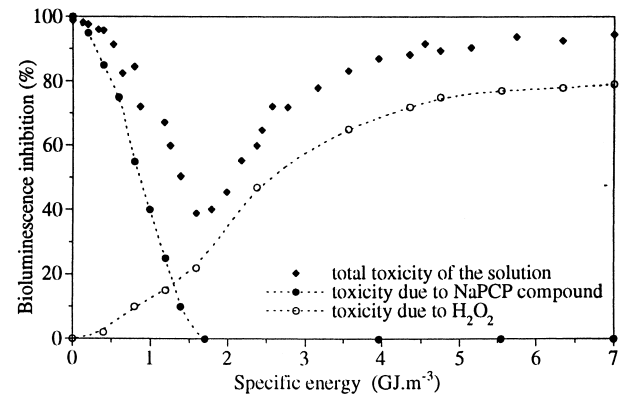

Fig. 10. Evolution of total toxicity and parts of toxicity due to NaPCP compound and hydrogen peroxide versus dissipated specific energy. The increase in toxicity has been attributed to hydrogen peroxide produced by water sonolysis.

sipated specific energy ($E_V = P_{th}/Vt$) which allows the bringing together of experiments carried out at different power densities. Thus the total toxicity of the solution is obtained along with the average toxicity of all the experiments (Figs. 5, 6 and 8). Toxicity due to the sodium pentachlorophenate compound, 'NaPCP compound', only was calculated from the evaluated NaPCP concentration (Fig. 2) and the calibration curve of the toxicity test (Fig. 4). In the same way, toxicity due to H_2O_2 was calculated from the measurement of H_2O_2 concentration (Fig. 8) and the respective calibration curve of the toxicity test (Fig. 4). The total toxicity of the samples is the result of the toxicities of all the compounds present in the solution, so there is a competition between the decrease in NaPCP toxicity and the increase in the toxicities of the products. During the first step in degradation, toxicity is essentially due to NaPCP, and beyond a specific energy of 1.5 GJ m^{-3}, it becomes negligible. Then, the solution toxicity is due to the products formed by ultrasound, and in particular, hydrogen peroxide. Note that the increase in toxicity (zone C and zone D) is not perceptible in Fig. 7. Indeed, after 10 h, samples diluted 10 times are non-toxic: after a 10 h treatment at a power density of 130 kW m^{-3} and specific energy equal to 4.68 GJ m^{-3}, the solution concentration is 1.5 mmol H_2O_2 l^{-1} (Fig. 9), so the concentration of samples diluted 10 times would be 0.15 mmol H_2O_2 l^{-1}, and therefore, the samples would be non-toxic (Fig. 4).

Nevertheless, in most of the experiments, the total toxicity seemed to be slightly higher than the added toxicities due to NaPCP and H_2O_2. This residual toxicity indicates, perhaps, the presence, in small quantities, of compounds produced from the ultrasonic degradation of pentachlorophenate which seem to resist ultrasound. Indeed, some analysis realized by mass spectrometry coupled with liquid chromatography exhibited, besides the degradation products like tetrachlorohydroquinone and tetrachlorobenzoquinone, the presence of other molecules with a much higher molecular weight (>400 g mol^{-1}) [27]. These polycycles could not have been clearly identified but they may be responsible for the residual part of toxicity. Another explanation for the differences between these toxicities (total and H_2O_2 toxicity) lie in the unknown factors in biological experiments.

3.2.2. Toxicity effects on daphnids

Toxicity evolution monitored by the test on daphnids confirms the previous results obtained with marine bacteria. Fig. 11 shows a similar evolution of toxicity for both tests even when the daphnids seem to be slightly less sensitive to the toxicity of the products (H_2O_2) than to NaPCP toxicity.

3.3. Effects of ultrasonic irradiation on biodegradability

The results of the biodegradability test are summarized in Fig. 12 which presents the evolution of toxicity in nine

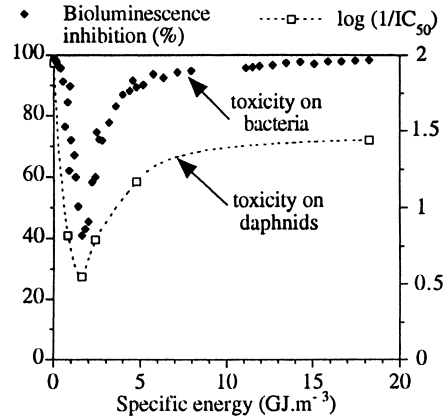

Fig. 11. Measurement of toxicity effects on daphnids: comparison with the toxicity effects on marine bacteria during the sonication of a pentachlorophenate solution.

samples for a period of 28 days. The first eight samples were taken after eight different irradiation exposure periods (0, 30 min, 1 h, 1.5 h, 2 h, 3 h, 4 h and 5 h at a power density of 220 kW m^{-3}) and inoculated with activated sludge. The last sample was a NaPCP solution without sludge. The reference used was bioluminescence inhibition of water (without PCP) inoculated with activated sludge and measured for 28 days. The toxicities indicated in Fig. 12 are the difference between the sample and the reference inhibitions. For no or low dissipated ultrasonic energy (sonication time between 0–1.5 h), the toxicity of the solutions remained too high to keep microorganisms alive since no development was seen in the bacteria population. The toxic compounds were therefore, not biodegraded. But after a sonication period longer than 2 h (which corresponds to a dissipated energy of 1.6 GJ m^{-3}), toxicity became low enough to be harmless for the bacteria. We can suppose that non-toxic compounds are biodegraded with a development in the bacterial population. Hence ultrasonic treatment is indispensable for sludge survival. Furthermore, non-toxic compounds formed by ultrasonic irradiation seem to be

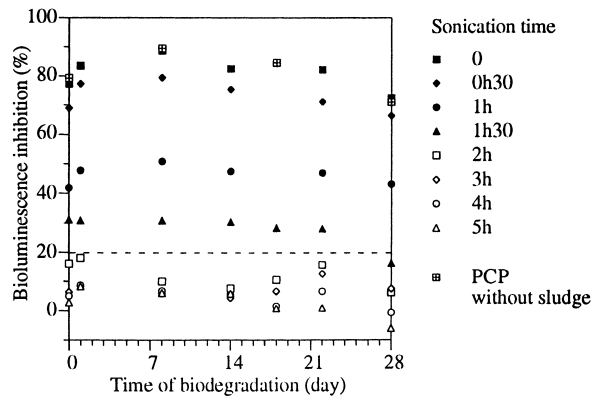

Fig. 12. Measurement of the biodegradability of the NaPCP solution after different periods of sonication.

degraded by the sludge. This test confirms that a biological treatment can be used after an ultrasonic irradiation in spite of the residual toxicity due to hydrogen peroxide.

4. Conclusions

From among all the uses of power ultrasound, wastewater treatment appears to be an original and expanding field of study. This process is convenient and simple in terms of temperature, pressure (ambient conditions) and reagents (no reagents). But more work is still necessary before the industrialization of the same. The conclusion drawn by some other authors is in agreement with those suggested by our own previous results: the energy consumption for total pollutant mineralization is very high. The ultrasonic process is, therefore, considered a preoxidation step. Hence it may be used at the outlet of industries to directly treat the concentrated wastewater before discharging it into a classical wastewater treatment plant.

The results related in this paper demonstrate that ultrasonic irradiation decreases the toxicity of a sodium pentachlorophenate solution immensely. Indeed, without ultrasonic pretreatment, the NaPCP solution would remain non-degradable by the sludge during the whole of the experiment (28 days).

5. Nomenclature

I	luminous intensity
CR	Control Ratio
k_{th}	kinetic pseudo-first-order rate constant ($m^3\ J^{-1}$)
[NaPCP]	sodium pentachlorophenate concentration (mol m^{-3})
P_{th}	thermal power measured by calorimetry (W)
t	time (s)
V	total volume of the solution (m^3)

Subscripts:

0	initial
t	exposure period (min)
b	blank
e	sample

References

[1] Y.Y. Lur'e, P.F. Kandzas, A.A. Mokina, Russian J. Phys. Chem. 36 (1962) 1422.
[2] J.W. Chen, J.A. Chang, G.V. Smith, Chem. Eng. Prog. Symp. Ser. 67 (1970) 18.
[3] F.O. Schmitt, C.H. Johnson, A.R. Olson, J. Am. Chem. Soc. 51 (1929) 370.
[4] S. Liu, H. Wu, J. Am. Chem. Soc. 56 (1934) 1005.
[5] K. Makino, M.M. Mossoba, P. Riesz, J. Am. Chem. Soc. 104 (1982) 3539.
[6] J.M. Wu, H.S. Huang, C.D. Livengood, Environ. Prog. 11 (1992) 195.
[7] A. Henglein, C. Kormann, Int. J. Radiat. Biol. 48 (1985) 251.
[8] T. Lepoint, F. Mullie, Ultrasonics Sonochem. 1 (1994) S13.
[9] N. Voglet, F. Mullie, T. Lepoint, New J. Chem. 17 (1993) 519.
[10] I. Hua, R.H. Höchemer, M.R. Hoffmann, J. Phys. Chem. 99 (1995) 2335.
[11] M.R. Hoffmann, I. Hua, R. Höchemer, Ultrasonics Sonochem. 3 (1996) S163.
[12] E. Gonze, Y. Gonthier, P. Baldo, A. Bernis, Can. J. Chem. Eng. 75 (1997) 245.
[13] N. Gondrexon, Thèse de l'Université de Savoie, Chambéry, France, 1994.
[14] E. Gonze, Y. Gonthier, P. Boldo, A. Bernis, Entropie 204 (1997) 21.
[15] E. Gonze, Y. Gonthier, P. Boldo, A. Bernis, Chem. Eng. Sci. 53 (1998) 523.
[16] V. Renaudin, N. Gondrexon, P. Boldo, C. Pétrier, A. Bernis, Y. Gonthier, Ultrasonics Sonochem. 1 (1994) S81.
[17] A. Francony, Thèse de l'Université de Savoie, Chambéry, France, 1995.
[18] M. Cost, G. Mills, P. Glisson, J. Lakin, Chemosphere 27 (1993) 1737.
[19] A. Bhatnagar, H.M. Cheung, Environ. Sci. Technol. 28 (1994) 1481.
[20] W.J. Catallo, T. Junk, Waste Manage. 15 (1995) 303.
[21] T.M. Olson, P.F. Barbier, Water Res. 28 (1994) 1383–1391.
[22] C. Pétrier, A. Jeunet, J.-L. Luche, G. Reverdy, J. Am. Chem. Soc. 114 (1992) 3148.
[23] C. Pétrier, M. Micolle, G. Merlin, J.-L. Luche, G. Reverdy, Environ. Sci. Technol. 26 (1992) 1639.
[24] A. Francony, C. Pétrier, Ultrasonics Sonochem. 3 (1996) S77.
[25] C. Pétrier, A. Francony, Water. Sci. Technol. 35 (1997) 175.
[26] R. Hiller, S.J. Putterman, B.P. Barber, Phys. Rev. Lett., Am. Chem. Soc. 69 (1992) 1182.
[27] E. Gonze, Thèse de l'Université de Savoie, Chambéry, France, 1996.
[28] C. Pétrier, M.-F. Lamy, A. Francony, V. Renaudin, N. Gondrexon, B. David, A. Benahcene, J. Phys. Chem. 98 (1995) 10514.
[29] J. Berlan, F. Trabelsi, H. Delmas, A.M. Wilhelm, J.-F. Petrignani, Ultrasonics Sonochem. 1 (1994) S97.
[30] N. Serpone, R. Terzian, H. Hidaka, E. Pelizzetti, J. Phys. Chem. 98 (1994) 2634.
[31] A. Kotronarou, G. Mills, M.R. Hoffmann, Environ. Sci. Technol. 26 (1992) 1460.
[32] A. Kotronarou, G. Mills, M.R. Hoffmann, J. Phys. Chem. 95 (1991) 3630.
[33] M.-F. Lamy, Thèse de l'Université de Savoie, Chambéry, France, 1994.
[34] I. Hua, M.R. Hoffmann, Environ. Sci. Technol. 30 (1996) 864.
[35] K. Inazu, Y. Nagata, Y. Maeda, Chem. Soc. Jpn, Chem. Lett. (1993) 57.