Wet peroxide degradation of atrazine

Eva M. Rodríguez, Pedro M. Álvarez, F. Javier Rivas [*],
Fernando J. Beltrán

*Departamento de Ingeniería Química y Energética, Facultad de Ciencias, Universidad de Extremadura,
Avenida de Elvas S/N, 06071 Badajoz, Spain*

Abstract

The high temperature (150–200 °C), high pressure (3.0–6.0 MPa) degradation of atrazine in aqueous solution has been studied. Under these extreme conditions atrazine steadily hydrolyses in the absence of oxidising agents. Additionally, oxygen partial pressure has been shown not to affect atrazine degradation rates. In no case mineralisation of the parent compound was observed. The addition of the free radical generator hydrogen peroxide to the reaction media significantly enhanced the depletion rate of atrazine. Moreover, partial mineralisation of the organics was observed when hydrogen peroxide was used. Again, oxygen presence did not influence the efficiency of the promoted reaction. Consecutive injections of hydrogen peroxide throughout the reaction period brought the total carbon content conversion to a maximum of 65–70% after 40 min of treatment (suggesting the total conversion of atrazine to cyanuric acid). Toxicity of the effluent measured in a luminometer decreased from 93% up to 23% of inhibition percentage. The process has been simulated by means of a semi-empirical model.
© 2003 Elsevier Ltd. All rights reserved.

1. Introduction

The increasing use of herbicides in agriculture, non-cropped industrial lands and on fallow lands has led to the inevitable contamination of the natural raw waters. Thus, post-application seasonal concentrations of different herbicides have been reported to exceed the maximum contaminant level permitted for surface waters (Nelson and Jones, 1994).

Broadly speaking, herbicides show rather low water solubility values and, in most of cases, they are toxic for microorganisms. As a result, conventional biological remediation processes are not suitable to remove these substances from contaminated water and tertiary treatments are required.

Adsorption on activated carbon is so far the preferred technology to deal with herbicides in drinking water plants. Thus, a number of studies have been reported on the use of this method both in bench and pilot scale (Baldauf, 1993; Gicquel et al., 1997; Thacker et al., 1997; Baup et al., 2000). Also, data can be found for water supply plants (Griffini et al., 1999). Adsorption on activated carbon is an efficient method showing high levels of pollutant removal at acceptable rates. However, it is also an expensive technology demanding a feasible and cost-effective carbon regeneration step, able to eliminate the adsorbates from the exhausted carbon surface without significant loss in adsorption capacity.

Among the technologies established for activated carbon regeneration purposes, the thermal treatment is widely used in most common applications, nevertheless,

[*] Corresponding author. Fax: +34-924-271304.
E-mail address: fjrivas@unex.es (F.J. Rivas).

a continuous loss of 5–15% of the initial carbon amount is experienced per regeneration cycle (Sheintuch and Matatov-Meytal, 1999). An emerging technology which uses milder conditions than the thermal regeneration is the wet air regeneration. This process consists of two steps. In the first stage (desorption) pollutants are steadily transferred to the aqueous phase by means of elevated temperatures and pressures typically found in this environment (Mishra, 1995). In the second stage, organics are oxidised to non-adsorbable and harmless polar compounds or, finally mineralised to carbon dioxide and water. In the later case, re-adsorption of oxidised intermediates is obviously avoided and complete regeneration of the activated carbon is expected. Additionally, regeneration of AC may be accomplished onto the surface of the solid, so the desorption stage is not needed. For these type of processes use of oxidation catalysts supported onto the AC surface can also be used (Sheintuch and Matatov-Meytal, 1999).

Although the wet air regeneration has been reported as a promising alternative to recover exhausted activated carbon, information on the oxidation kinetics of desorbed species is scarce. In this sense, most of wet oxidation studies have been focused on the kinetics of aromatic compounds, with special emphasis on phenol type substances, and to a lesser extent on other chemical structures (aliphatics, inorganics, etc.) (Mishra, 1995).

No studies are found in the past and recent literature on the main features on pesticide wet air oxidation. Thus, if carbon regeneration is meant to be completed by the wet air process, the behaviour of pesticides in this environment should be previously assessed. Therefore, in the present work, the wet air oxidation of atrazine has been carried out. Also, the promoted oxidation of atrazine by hydrogen peroxide has been considered. Hydrogen peroxide is known to directly generate highly reactive species capable of oxidasing most of organics in a non-selective way (Rivas et al., 1999).

Atrazine is a selective *s*-triazine herbicide used to control broadleaf and grassy weeds in different crops. Because it does not adsorb strongly to soil particles and has a lengthy half-life, it has a high potential for groundwater contamination despite its moderate solubility in water (Briggs, 1992).

2. Experimental

2.1. Experimental apparatus and procedures

Experiments were completed in a 600 cm^3, 316 stainless-steel autoclave operated in batch mode. Reactor walls were lined with a PTFE layer so the only metallic surface in contact with the reaction media was the stirrer. Runs were carried out over a temperature and total pressure ranges of 150–200 °C and 3.0–6.0 MPa, re-

spectively. The system was pressurised directly from a gas cylinder containing either nitrogen or air. The operating procedure was as follows: 350 cm^3 of an unbuffered atrazine aqueous solution (≈ 2–4×10^{-4} M) was placed in the batch reactor and the system pressurised to 1.0 MPa. Then, the stirrer was initiated and the reactor heated to the required operating temperature. When the desired temperature was achieved, typically in less than 15 min, the pressure was adjusted at the predetermined working conditions using the gas cylinder pressure. This time was taken as time zero. At appropriate intervals, a sample was withdrawn from the reactor. The sampling line was initially flushed twice with a quantity of liquid equivalent to the sample line volume (2 ml). The sample was cooled in the sampling line prior to pressure let-down to prevent flashing of the liquid across the valve. Following sampling, reactor pressure was restored to the initial value.

For hydrogen peroxide promoted experiments, commercial 33% H_2O_2 was used to prepare the appropriate solutions. Five millilitres of the previous solutions were injected by means of a stainless steel cylinder coupled to the autoclave once the working temperature had been attained. Therefore decomposition of this reagent before time zero was prevented. The hydrogen peroxide concentration at time zero oscillated in the range 1×10^{-4} to 10^{-2} M.

2.2. Analytical methods

Atrazine and first degradation intermediates (deethylatrazine, deisopropylatrazine and deethyldeisopropylatrazine) were obtained from Dr. Ehrenstorfer laboratory (D 86199 Augsburg, Germany) and used as received. The concentration of atrazine was monitored with a Hewlett-Packard HPLC system equipped with a 1100 Series pump, an injector and a UV–VIS detector set at 220 nm. In each run, 20 µl of sample was injected via an automatic injection system. The mobile phase (flow-rate 1.0 cm^3 min^{-1}) was a solution of 40/60 v/v acetonitrile–water and the stationary phase was a Nova-Pack C18 column (Waters, 150 × 3.9 mm). The detector was set at 210 nm. The separation was made with the following acetonitrile–water gradient elution program: at room temperature, 100% of pH 7.2 buffered pure water (Milli Q, Millipore) at time 0 for 3 min, 87% by vol. up to 11 min and 60% by vol. up to 30 min, with a flow rate of 1.0 cm^3 min^{-1}. Total carbon (TC) was analysed by means of a Dohrmann DC-190 carbon analyser.

3. Results and discussion

3.1. Hydrolysis of atrazine

In a first stage the wet degradation of atrazine was conducted under an inert atmosphere of nitrogen to
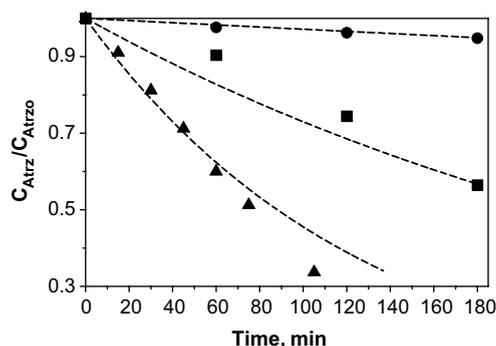
Fig. 1. Wet degradation of atrazine under inert atmosphere. Influence of temperature on atrazine conversion. Experimental conditions: $P_T = 6.0$ MPa, pH = 5–6, $C_{atrazo} = 2 \times 10^{-4}$ M (average value). (▲) 200 °C; (■) 185 °C; (●) 150 °C (dotted lines = model calculations).

Fig. 2. Wet air degradation of atrazine. Influence of oxygen partial pressure on atrazine conversion. Experimental conditions: $T = 200$ °C, pH = 5–6, $C_{atrazo} = 2 \times 10^{-4}$ M (average value). (◆) $P_T = 4.0$ MPa (air); (■) $P_T = 6.0$ MPa (air); (●) $P_T = 6.0$ MPa (nitrogen).

ascertain the existence of non-oxidative reactions leading to the parent compound disappearance from the media. Thus, experiments were carried out in the absence of oxygen in the temperature range from 150 to 200 °C. Fig. 1 depicts the evolution of the normalised remaining atrazine concentration with time for this experimental series. As inferred from this plot, some non-oxidative processes develop leading to atrazine depletion. Given the conditions used in this set of experiments, hydrolysis of atrazine (I) to form hydroxy-atrazine (II) (6-hydroxy-*N*-2-ethyl-*N*-4-isopropyl-1,3,5-triazine-2,4-diamine) is likely to occur (Widmer et al., 1993). Also, as expected, no change in the total carbon content (TC) was experienced in the absence of oxidising agents.

3.2. Effect of oxygen partial pressure

The following step, considered in this study, was to assess the effect of oxygen presence on both atrazine and TC conversion rates. Consequently, a series of experiments was conducted at different air total pressure and the results compared to similar runs completed under nitrogen atmosphere. Fig. 2 shows the experimental atrazine conversions obtained when working at 4.0 and 6.0 MPa by using either air or nitrogen. As observed from this plot, at the conditions used in this work, oxygen addition did not result in the enhancement of the process in terms of atrazine removal. Moreover, TC remained unvaried throughout the reaction regardless of the oxygen partial pressure used. This indicates that oxygen was unable to attack either atrazine and/or hydroxyatrazine and, subsequently, begin the typical radical chain mechanism developed in wet air oxidation processes, eventually leading to the partial mineralisation of the parent compound.
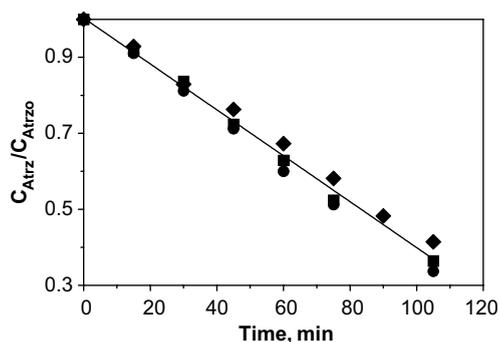
3.3. Effect of hydrogen peroxide addition

Based on the previous results, it was decided to study the influence of the addition of a free radical generator to the reaction media. Therefore, hydrogen peroxide influence was tested by injecting this species into the reactor at concentration values ranging from 0 to 0.01 M.

Fig. 3 shows the effect of hydrogen peroxide addition on atrazine elimination profiles. As inferred from this plot, a significant enhancement of the process was experienced at increasing doses of this reagent. At the sight of the curves found for the normalised atrazine concentration profiles, it is observed how the decay rate of the herbicide slows down as the reaction progresses. Thus, from Fig. 3 it can be seen how after the initial fast degradation stage (oxidation due to radical species),
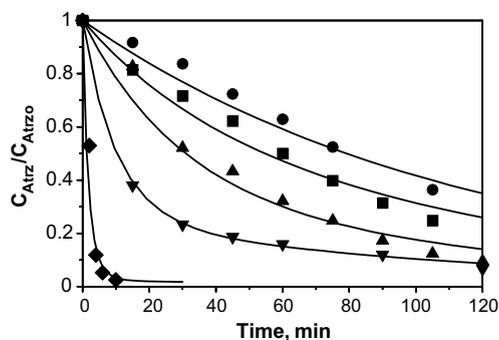

Fig. 3. Wet air degradation of atrazine. Influence of hydrogen peroxide addition on atrazine conversion. Experimental conditions: $P_T = 6.0$ MPa (air), $T = 200$ °C, pH = 5–6, $C_{atrazo} = 2 \times 10^{-4}$ M (average value). (●) $C_{H_2O_2 o} = 0.0$ M; (■) $C_{H_2O_2 o} = 10^{-4}$ M; (▲) $C_{H_2O_2 o} = 5 \times 10^{-4}$ M; (▼) $C_{H_2O_2 o} = 10^{-3}$ M; (◆) $C_{H_2O_2 o} = 10^{-2}$ M (lines = model calculations).

atrazine depletion rate levels off to values below the rate expected for a zero order kinetics if hydrolysis followed this type of rate law, i.e. in case of a zero order kinetics a faster elimination rate would develop after hydrogen peroxide consumption has been achieved. As a consequence, it might be considered that the thermal degradation of atrazine does follow a first order kinetics.

3.4. Kinetic modelling

In the presence of added hydrogen peroxide, the high temperature, high pressure degradation of aqueous atrazine was modelled by considering the mechanism presented in Scheme 1. In the adopted reaction mechanism, atrazine (I) is considered to react with water (hydrolysis) or with hydroxyl radicals to yield the chloride substitution (hydroxyatrazine, II), isopropyl group removal

(deisopropylatrazine, VI) or ethyl group removal (deethylatrazine, V). Subsequent reactions of these intermediates may lead to complete elimination of substituents to finally give cyanuric acid (VIII) and low molecular weight final products. Cyanuric acid is one of the refractory substances found in the oxidation processes and it eventually accumulates in the reaction media (Beltrán et al., 2000). Nevertheless, according to literature data, this compound has been demonstrated to be non-toxic (Canelli, 1974).

In the mechanism, thermal decomposition of atrazine has been assumed to proceed through simple first order kinetics. Also, hydrogen peroxide has been considered to undergo homolytic excision to generate two hydroxyl radicals, capable of degrading atrazine (reaction 1). The value assumed of k_{per} was first taken from a previous work (Rivas et al., 1999) although fitting of this
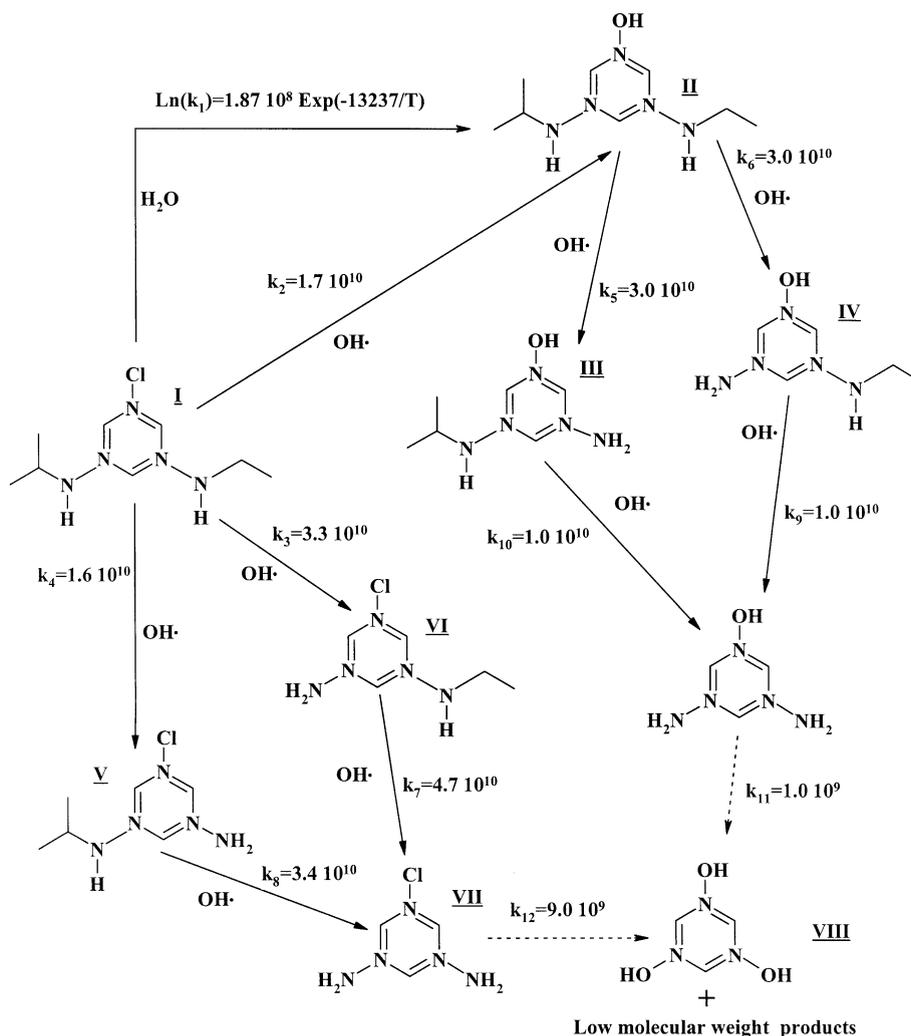
Scheme 1. Proposed mechanism for the wet peroxide oxidation of atrazine.

parameter resulted in a slightly lower value (the fitting session was made by just considering atrazine degradation profiles). Ineffective reaction of hydrogen peroxide decomposition leading to non-oxidative species has also been taken into account by means of an apparent constant k_{ineff} (reaction 2). The later reaction includes elementary steps like radical–radical termination, injection effects producing local high concentrations of hydrogen peroxide which, at these conditions, would act as an scavenger of hydroxyl radicals, radical deactivation against the reactor wall, etc.

$$H_2O_2 \rightarrow 2OH^{\cdot} \quad k_{Per} \tag{1}$$

$$H_2O_2 \rightarrow 1/2 O_2 + H_2O \quad k_{ineff} \tag{2}$$

In a first attempt, the rate constant of atrazine hydrolysis was obtained by fitting experimental results acquired in experiments completed in the absence of hydrogen peroxide. The fitting process was carried out by a computer software using the evolutionary programming (EP) which is a computational technique that mimics evolution and is based on reproduction and selection (Bäck et al., 1993; Mendes and Kell, 1998). Fig. 1 shows the computed evolution of atrazine with time (dashed lines) after the adjustable parameter k_1 was optimised. The Arrhenius analysis of this parameter allowed for the calculation of the pre-exponential factor and activation energy of the reaction. Thus, the following expressions was obtained: $k_1 = 1.87 \times 10^8 \exp(-13237/T) \text{ s}^{-1}$. Hydrolysis of atrazine has been studied at room temperature and no available data was found at high temperature. Extrapolation of data at ambient conditions by means of the Arrhenius equation obtained is somehow audacious. However the attempt was conducted and the value of k_1 calculated did corroborate the persistence of this herbicide at circumneutral pH and room temperature. Thus Widmer et al. (1993) gave a value of around $4.9 \times 10^{-13} \text{ s}^{-1}$ for a temperature range 4–30 °C. In this work a value of $2.8 \times 10^{-12} \text{ s}^{-1}$ was obtained when using the Arrhenius expression for a temperature of 17 °C.

Kinetic constants k_{Per} and k_{ineff} are known to be highly dependent on the nature and geometry of the reactor (Rivas et al., 1998). Several values have been reported in the literature (Shibaeva, 1969; Rivas et al., 1999). In this work, an average value (after the fitting process) of 10^{-4} s^{-1} has been assumed for k_{Per}. As stated previously, this value is lower than those reported for the decomposition of hydrogen peroxide in the wet air oxidation environment (Shibaeva, 1969; Rivas et al., 1999). The reason of this lower value of k_{Per} is based on the use of a reactor surface made of PTFE, which is more inert than the metallic surface reported by the aforementioned authors.

Once k_1 and k_{Per} were established, the rest of the unknown rate constants were simultaneously evaluated

by EP. To start with the computational method initial guess of rate constants should be accomplished. Initial values of some rate constants of the reactions between organics and hydroxyl radicals were taken from the literature at room temperature (Beltrán et al., 2000). When no available data could be found for rate constants a generic value of $5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ was assumed (Buxton et al., 1988). As observed from Scheme 1 presented, the values of the rate constants between the hydroxyl radical and the organic species are slightly above than those reported at room conditions (Beltrán et al., 2000). Thus, typical values reported for *s*-triazines and hydroxyl radicals are in the interval $1–5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. The one fold higher order obtained in the regression analysis may be attributable to the higher temperature conditions used in the WAO environment. It should be noticed that the increase in the values of these constants is not significant if compared (or expected) to differences in working temperatures. This is due to the low activation energy of the reactions of the hydroxyl radical, (i.e. typical activation energies for hydroxyl radical reactions are close to 5 kJ/mol, confirming the magnitude of rate constants calculated in the fitting process).

Subsequently, atrazine and intermediate theoretical concentration profiles were determined and compared to the experimental results obtained in the various runs conducted in the presence of hydrogen peroxide. Fig. 3 shows the computed results (solid lines) of atrazine concentration profiles obtained after optimisation of the value of adjustable rate constants. As seen from this plot, the model does a good job when simulating the atrazine depletion with time. Also, Fig. 4 depicts the experimental and computed intermediate concentrations identified in this work for a run completed with 0.01 M of hydrogen peroxide. As observed, the reaction mechanism proposed simulates quite well the main
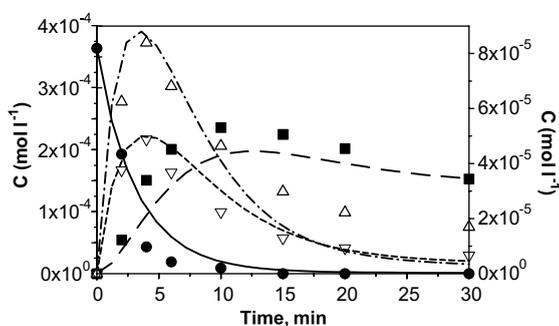
Fig. 4. Wet air degradation of atrazine. Influence of hydrogen peroxide addition on atrazine conversion and intermediates formation. Experimental conditions: $P_T = 6.0$ MPa (air), $T = 200$ °C, pH = 5–6, $C_{atrazo} = 3.6 \times 10^{-4}$ M, $C_{H_2O_2\,o} = 10^{-2}$ M. (●, —), Atrazine; (∇, - - - -), Deethylatrazine; (Δ, —·—·—), Deisopropylatrazine; (■, – – –), Deethyldeisopropylatrazine (symbols = experimental results, lines = model calculations).

by-product concentration profiles, i.e. deethylatrazine, deisopropylatrazine and deethyldeisopropylatrazine. Validation of the reaction mechanism was conducted by testing the kinetic model at different conditions of initial atrazine concentration (Fig. 5A) and initial hydrogen peroxide concentration (Fig. 5B).

As stated before, from the fitting process the value of k_{ineff} could be obtained. Given the empirical definition of this apparent rate constant, accounting for several elementary steps, its value changed as the concentration of hydrogen peroxide was varied. Nevertheless, a simple power expression could be applied to relate k_{ineff} and the initial hydrogen peroxide concentration used, $k_{ineff} = \alpha[H_2O_2 o]^n$. After linearisation, by applying the natural logarithm to both sides of the previous expression, the

following equation was obtained, $Ln(k_{ineff}) = -4.41 + 0.40 Ln(H_2O_2)$. It has to be pointed out that values obtained for k_{ineff} are of equal magnitude than those reported for a similar system like Fenton's reagent (Rivas et al., 2002) with the corresponding divergences attributable to differences in working temperature. A sensitivity analysis of the proposed mechanism demonstrated that the limiting reactions were the atrazine hydrolysis and hydrogen peroxide decomposition. The values of the rest of kinetic parameters is not of paramount importance as far as they are considered in the normal range of values for the reaction between the hydroxyl radical and organic species (considering the high operating temperature). Nevertheless, these values of the rate constants should be taken with caution since they have been obtained by means of an optimisation process and have to be considered as a mere approach to the actual values.

Again the presence of oxygen was tested for experiments initiated by hydrogen peroxide. A series of experiments was therefore carried out at different air total pressure (range = 3.0–6.0 MPa) and under nitrogen atmosphere by adding the same amount of the promoter/generator at the beginning of the reaction. Two sets of runs were completed with 10^{-2} and 10^{-3} M of H_2O_2. The experimental results (not shown) established that oxygen had not influence either on the final atrazine removal or TC conversion, therefore discarding the development of a chain mechanism involving organic radical species. Some small differences found in atrazine conversion (±10%) did not follow a clear trend and could be due to sampling effects, even after flushing the sampling port twice before a sample was taken for analysis. The evolution of TC followed a parallel behaviour to that expected for the hydrogen peroxide concentration and consequently for the hydroxyl radicals present in the reaction media. In Fig. 6 experimental TC conversion and theoretical H_2O_2 and $HO^{\cdot}$ radicals concentrations are plotted for the experiment carried out when adding 10^{-2} M of the radical generator. As seen from this figure, once hydrogen peroxide has disappeared, TC conversion reaches a plateau of roughly 35% with no further elimination after 90 min of treatment.

To ascertain if the TC plateau could be attributed to the absence of H_2O_2 or, contrarily, to the accumulation of refractory species to the action of the oxidant, some experiments were then carried out by adding different amounts of H_2O_2 in successive steps throughout the reaction period. As seen in Fig. 7, injection of additional amounts of hydrogen peroxide (10^{-2} M) to the reaction media led to a significant improvement of the process in terms of TC final depletion. Therefore, the plateau reached for the TC conversion in experiments carried out with a single H_2O_2 injection was likely due to the disappearance of this reagent at the beginning of the process. In any case, no important differences were ex-
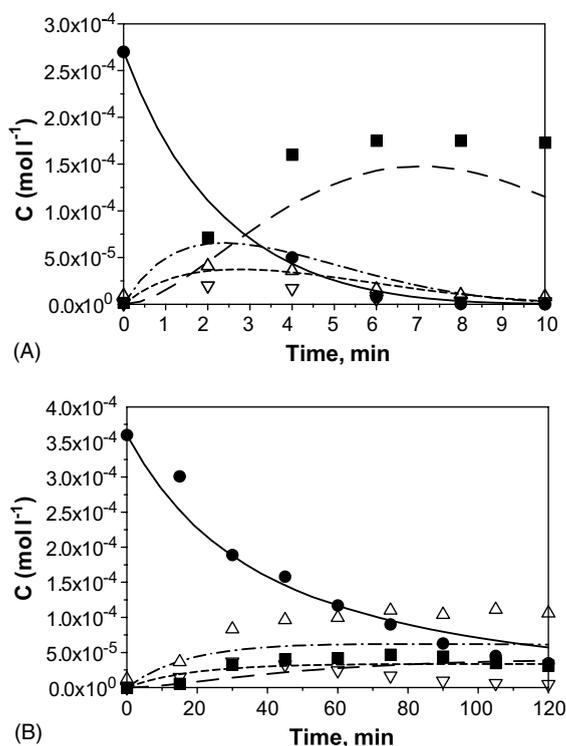

Fig. 5. (A) Wet air degradation of atrazine. Influence of hydrogen peroxide addition on atrazine conversion and intermediates formation. Experimental conditions: $C_{atrazo} = 2.7 \times 10^{-4}$ M, $C_{H_2O_2 o} = 10^{-2}$ M, $P_T = 6.0$ MPa (air), $T = 200$ °C, pH = 5–6. (●, ——), Atrazine; (∇, - - - -), Deethylatrazine, (△, –·–·–), Deisopropylatrazine; (■, ——), Deethyldeisopropylatrazine (symbols = experimental results, lines = model calculations). (B) Wet air degradation of atrazine. Influence of hydrogen peroxide addition on atrazine conversion and intermediates formation. Experimental conditions: $C_{atrazo} = 3.6 \times 10^{-4}$ M, $C_{H_2O_2 o} = 5 \times 10^{-4}$ M, $P_T = 6.0$ MPa (air), $T = 200$ °C, pH = 5–6. (●, - - -), Atrazine; (∇, - - - -), Deethylatrazine; (△, –·–·–), Deisopropylatrazine; (■, ——), Deethyldeisopropylatrazine (symbols = experimental results, lines = model calculations).
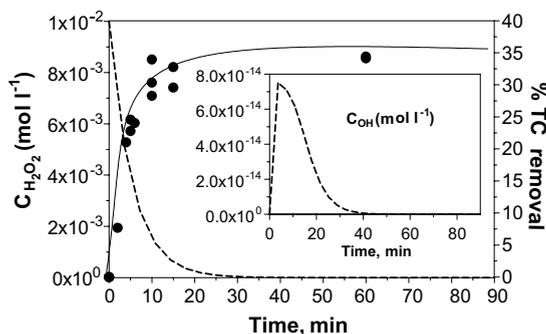
Fig. 6. Wet air degradation of atrazine in the presence of hydrogen peroxide. Evolution of experimental TC (solid line + circle symbols), theoretical H_2O_2 (dotted line) and theoretical HO· radicals (embedded figure) with time. Experimental conditions: $P_T = 6.0$ MPa (air or nitrogen), $T = 200$ °C, pH $= 5$–6, $C_{atrazo} = 3.6 \times 10^{-4}$ M, $C_{H_2O_2 \, o} = 10^{-2}$ M, $TC_o = 22$ mg l^{-1}.
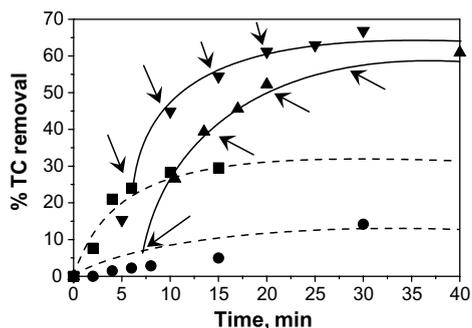

Fig. 7. Wet air degradation of atrazine in the presence of hydrogen peroxide. Evolution of experimental TC with time after several injections of hydrogen peroxide (10^{-2} M). Conditions as in Fig. 6. Arrows indicate the time at which 10^{-2} M of a fresh solution of H_2O_2 was injected. (■) 200 °C single injection; (▼) 200 °C multiple injection; (●) 150 °C single injection; (▲) 150 °C multiple injection.

perienced after the last injection of H_2O_2. Hence, it can be postulated that after a given amount of H_2O_2 has been injected to the system, accumulation of refractory substances occurs and no further conversion of TC is achieved. The drop in pH (roughly 2 units) attained at the end of the oxidation process suggests the formation of HCl from the original atrazine molecule (either by hydrolysis or direct attack of the hydroxyl radical to the chloro position). Although speculative in nature (cyanuric acid has not been measured), it is worth to signify that the plateau reached in TC conversion (≈ 60–65%) roughly coincides with the theoretical decrease in TC calculated if all molecules of atrazine had transformed into cyanuric acid (62.5%). Also, it is noteworthy to say that temperature does not significantly affect TC final abatement. As stated previously, these results

could be expected since reactions of hydroxyl radicals are characterised by low activation energies, normally the generation of these species being the controlling step.

Toxicity of samples after hydrogen peroxide treatment was measured by using a luminometer (Tox-Alert®), this method based on the inhibition percentage of a bioluminiscent bacteria (*Vibrio fischeri* NRRL B-11177). The percentage of inhibition decreased from 93% untreated atrazine solution to 23% after oxidation which suggest the formation of the low toxic cyanuric acid.

4. Conclusions

On the basis of the above experimental findings on the wet air oxidation of atrazine the following conclusions may be drawn:

(i) Atrazine hydrolyses at high temperatures in the absence of any oxidising agent. Hydrolysis of the herbicide does not contribute to the removal of the organic load of the aqueous solution. Hydroxyatrazine likely accumulates in the reaction media and, as a consequence, it does not seem an appropriate environment for carbon regeneration since this metabolite probably re-adsorbs on the carbon surface.
(ii) The presence of oxygen does not enhance atrazine degradation rate and accumulation of hydrolysis products also occurs.
(iii) Addition of hydrogen peroxide results in a significant enhancement of the process. The use of this reagent also allows for the partial mineralisation of the parent compound, though TC depletion stops when the H_2O_2 added completely decomposes.
(iv) Consecutive injections of H_2O_2 at determined time intervals lead to a final TC conversion of roughly 65–70% with no further increase of this parameter after having injected a total amount of 5×10^{-2} M of H_2O_2. The high reduction of TC achieved and likely the accumulation of small polar acids in the media dictates that this technique should be suitable for spent carbon regeneration.
(v) Two factors might contribute to the economy of the process. On one hand, the amount of hydrogen peroxide used can be lowered since a negligible improvement of the TC conversion is obtained after the third injection. On the other hand, the use of spent carbon permits to achieve a concentration of atrazine in the WAO environment higher than the concentration reached after saturation at room temperature. Therefore, it is likely that hydrogen peroxide can be more effectively used reducing the fraction of this reagent leading to oxygen and water. Additionally, in a real plant, H_2O_2 should be fed

continuously, so no injection of this reagent is needed facilitating, therefore, the process.

Acknowledgements

References

Bäck, T., Fogel, D.B., Michalewicz, Z., 1993. Handbook of Evolutionary Computation. IOP Publishing/Oxford University Press, Oxford.

Baldauf, G., 1993. Removal of pesticides in drinking-water treatment. Acta Hydroch. Hydrob. 21 (4), 203–208.

Baup, S., Jaffre, C., Wolbert, D., Laplanche, A., 2000. Adsorption of pesticides onto granular activated carbon: determination of surface diffusivities using simple batch experiments. Adsorp. J. Int. Adsorp. Soc. 6 (3), 219–228.

Beltrán, F.J., González, M., Acedo, B., Rivas, F.J., 2000. Kinetic modelling of aqueous atrazine ozonation processes in a continuous flow bubble contact. J. Hazard. Mater. 80 (1–3), 189–206.

Briggs, S., 1992. A Basic Guide to Pesticides: Their Characteristics and Hazards. Hemisphere Publishing Corporation, Washington. pp. 8–9.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($^{•}$OH/$^{•}$O^{-}) in aqueous-solution. J. Phys. Chem. Ref. Dat. 17 (2), 513–886.

Canelli, E., 1974. Chemical, bacteriological and toxicological properties of cyanuric acid and chlorinated isocyanurates as applied to swimming pool disinfection. Am. J. Public Health 62, 155–162.

Gicquel, L., Wolbert, D., Laplanche, A., 1997. Adsorption of atrazine by powdered activated carbon: influence of dis-solved organic and mineral matter of natural waters. Environ. Technol. 18 (5), 467–478.

Griffini, O., Bao, M.L., Burrini, D., Santianni, D., Barbieri, C., Pantani, F., 1999. Removal of pesticides during the drinking water treatment process at Florence water supply, Italy. J. Water Serv. Res. Technol.-Aqua. 48 (5), 177–185.

Mendes, P., Kell, D.B., 1998. Non-linear optimization of biochemical pathways: applications to metabolic engineering and parameter estimation. Bioinformatics 14, 869–883.

Mishra, V.S., 1995. Wet air oxidation. Ind. Eng. Chem. Res. 34, 2–48.

Nelson, H., Jones, R., 1994. Potential regulatory problems associated with atrazine, cyanazine, and alachlor in surface-water source drinking-water. Weed Technol. 8 (4), 852–861.

Rivas, F.J., Kolaczkowski, S.T., Beltrán, F.J., McLurgh, D.B., 1998. Development of a model for the wet air oxidation of phenol based on a free radical mechanism. Chem. Eng. Sci. 53, 2575–2586.

Rivas, F.J., Kolaczkowski, S.T., Beltran, F.J., McLurgh, D.B., 1999. Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts. J. Chem. Technol. Biotechnol. 74 (5), 390–398.

Rivas, F.J., Beltrán, F.J., Gimeno, O., Ålvarez, P., 2002. Treatment of brines by combined Fenton reagent aerobic biodegradation. II. Process modelling. J. Hazard. Mater. B 96, 259–276.

Sheintuch, M., Matatov-Meytal, Y.I., 1999. Comparison of catalytic processes with other regeneration methods of activated carbon. Catal. Today 53 (1), 73–80.

Shibaeva, L.V., 1969. The oxidation of phenol with molecular oxygen in aqueous solutions. II. The role of hydrogen peroxide in the oxidation of phenol. Kinet. Catal. 10, 1022–1026.

Thacker, N.P., Vaidya, M.V., Sipani, M., Kalra, A., 1997. Removal technology for pesticide contaminants in potable water. J. Environ. Sci. Health B 32 (4), 483–496.

Widmer, S., Olson, J., Koskinen, W., 1993. Kinetics of atrazine hydrolysis in water. J. Environ. Sci. Health B 28 (1), 19–28.