WET OXIDATION BY HYDROGEN PEROXIDE FOR THE TREATMENT OF MIXED RADIOACTIVE AND TOXIC ORGANIC WASTES AND WASTE WATERS

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ABSTRACT. The experiments carried out on a complex organic mixture, simulating the radioactive organic wastes produced in an Italian nuclear fuel reprocessing plant, have demonstrated the effectiveness of the wet oxidation with the reduction of the organic matter up to 95% and a maximum consumption of 15 L of H_2O_2 to entirely oxidize 1 L of organic waste. Preliminary tests, moreover, on simulated waste waters containing toxic organic compounds have given good results: PCBs are destroyed up to 95% performing the wet oxidation process (WOX) in homogeneous media and atrazine degradation is complete. Finally, the Chemical Oxidation Demand (COD) values of olive vegetation water, waste waters with high non biodegradable phenolic content, are drastically decreased by WOX.

INTRODUCTION

Numerous toxic and nonbiodegradable organic compounds are often present in waste waters and their removal sometimes requires a careful and expansive design of the usual processes and new processes are often useful.

An innovative method to treat toxic and hazardous waste waters (1–4) and organic solvent wastes (5) is the wet oxidation process (WOX) at low temperature using hydrogen peroxide and catalysts. This process is simple, easy and safe, being carried out at relatively low pressure and low temperatures (up to 16 bar and 200°C) and producing essentially water and carbon dioxide as final products. On the other hand, the WOX which uses air or oxygen is a well-known process, but the severe operating conditions (pressure up to 250 bar and temperature greater than 300°C) have prevented its large-scale industrial development (6,7).

In a previous study (8) we have optimized the reaction conditions for the mineralization of an organic mixture, simulating the radioactive organic solvent produced at ENEA research reprocessing plants. The laboratory tests were carried out by using concentrated hydrogen peroxide-iron (II) salt (the

Fenton's reagent) at boiling temperature (~100°C) and vigorous stirring.

The aim of this work is to confirm the effectiveness of WOX in particular for its large-scale application in the treatment of nuclear organic wastes with experiments on a pilot plant, but also degradation of both real and simulated waste waters containing especially nonbiodegradable compounds.

EXPERIMENTAL

Chemicals

Polychlorinated biphenyls (PCBs) (Askarel oil for transformers) were supplied by Nucleo S.p.A. Hydrogen peroxide (36%, w/v) and iron (II) sulphate eptahydrate were obtained from Carlo Erba (Milan, Italy). Atrazine(2-chloro-4(ethylamino)-6(isopropylamino)-*s*-triazine), *s*-triazine herbicide, was purchased up to 99.1% from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Solvesso 100, a complex mixture composed principally of alkylaromatic hydrocarbons, was supplied by Esso Chemicals (Milan, Italy) and technical grade tri *n*-octylamine containing at least five long-chain Tertiary Aliphatic Amines (TAAs) by Chemical Procurement Co. (New York, U.S.A.). Solvents and reagents (analytical grade) were supplied by E. Merck (Darmstadt, Germany).

Apparatus

A Perkin Elmer Model 8510 Gas Chromatograph (GC) was used, in a version equipped with flame ionization detector and a Programmed Temperature Vaporizer (PTV) capillary column injector, built-in data handling with reintegration, connected with a GP-100 printer-plotter of the same trademark. The capillary column was a BP1 (12 m × 0.22 mm I.D., 0.25 μm film thickness) of Scientific Glass Engineering Co. Two analytical methods were used: 1) the oven temperature was held at 45°C for 17 min, then programmed at 8°C/min to 300°C and held (3 min); 2) the oven temperature was held at 110°C for 1 min, then programmed at 4°C/min to 270°C and held (0.5 min).

High-Performance Liquid Chromatography (HPLC) analyses were performed by using a Series 3B Liquid Chromatograph (Perkin Elmer) equipped with a LC-75 Spectrophotometric Detector (Perkin Elmer) connected to a Model 9176 Recorder (Varian). The analytical column (15 cm × 4.0 mm I.D.) was home packed with a Spherisorb S5 ODS2 (Phase Separation). A reversed phase guard column, filled with pellicular packing, was used to protect the analytical column. Eluition was operated with a methanol-water concentration gradient: from 50:50 v/v to 90:10 linearly in 15 min, then held for 4 min. The flow rate was maintained at 1 mL/min. The detection wavelength was set at 223 nm.

The total organic carbon analysis (TOC) was performed using a Carlo Erba Model 480-R Total Carbon Monitoring equipped with a Hewlett Packard 3396 A Integrator. The Chemical Oxygen Demand (COD) analyses was performed in accordance to ASTM method D1252-78 (9).

Methods

The details of the experiments are described in the "Results and Discussion" section under the headings of materials to which they refer. We have chosen this approach because the operating modes of experiments are different and typical for the treated material.

RESULTS AND DISCUSSIONS

Simulated Radioactive Organic Wastes

The experimental tests on radioactive organic solvent wastes were performed by using the pilot plant whose main features are shown in Fig. 1. The treated volume for each experiment was 5 L. The tests were executed charging the organic mixture in the glass reactor (total volume of 50 L) together with catalyst and heating it at about 100°C, by means of steam heating coil, at atmospheric pressure. Then hydrogen peroxide was fed at a maximum flow rate of 10 L/h. To increase the oxidation efficiency, the hydrogen peroxide feed and mechanical agitation were stopped every time the level in the reactor reached about 30 L. After a few minutes, the organic solution was separated by gravity from aqueous phase. This last, when the separation was complete, was manually drained by means of valve installed on the reactor bottom until about 5 L remained in reactor. Then, another rate of catalyst was added and the reaction started again for the treatment of the residual organic not yet oxidized. This cycle was repeated until the volume of organic phase didn't change.

The composition of the solvent waste utilized in the tests, was the following: TAA 293 g/Kg, Solvesso-100 85 g/Kg, tributyl phosphate (TBP) 383 g/
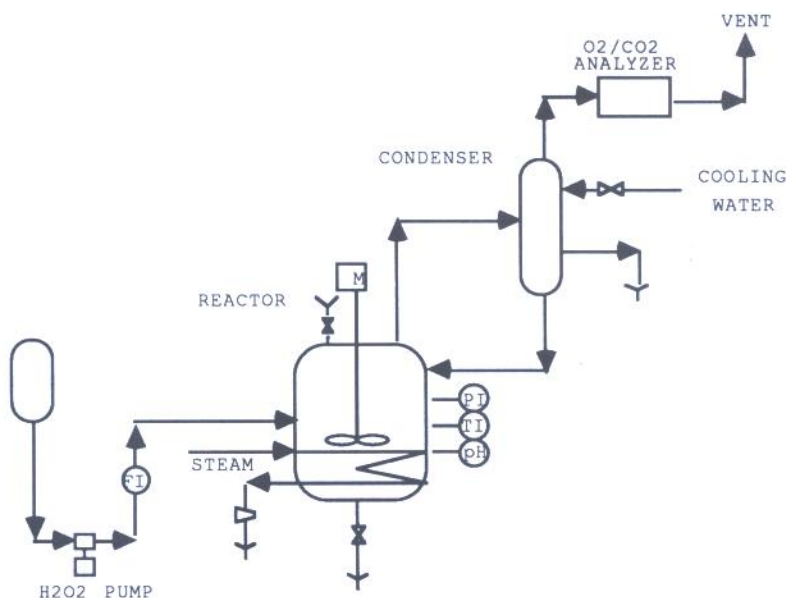

FIGURE 1. Pilot plant used for radioactive solvent waste treatment.

Kg, mesitylene (1,3,5 trimethylbenzene) 118 g/Kg, kerosene 121 g/Kg. The catalyst was $FeSO_4 \cdot 7H_2O$ with rate of 100 g per cycle. The oxidizing mixture was 36% H_2O_2 plus concentrated H_2SO_4 (15 mL/L). With the above characteristics of the feeds, the process was complete after three cycles, with an oxidant consumption of about 55 L.

The reaction final products were: 60 L of aqueous wastes, with an average COD of about 1 g/L, and 450 mL of organic wastes. In Fig. 2 is represented the reduction of the organic solvent volume. The degradation kinetics of TBP, mesitylene, amine (namely TAA_1), and kerosene, chromatographically parted in three principal components, are shown in Fig. 3. The curve related to Solvesso 100 is omitted because it decreases as well as mesitilene. Aromatic hydrocarbons, tertiary aliphatic amines, and alkyl groups of TBP are totally and easily decomposed to carbon dioxide and water. Alkanes, instead, are chemically inert to WOX. In the final organic mixture, in fact, there are only kerosene components and probably a preliminary treatment, as distillation or evaporation, is necessary to separate the low-boiling fraction inactive to WOX.

Polychlorinate Biphenyls (PCBs)

From the previous studies we experienced that the WOX is very effective to destroy numerous organic compounds. Therefore, we carried out laboratory tests to verify if the same treatment is effective to destroy PCBs. The Askarel oil utilized coincided with the Aroclor 1260 (10), containing principally PCBs with 5, 6, and 7 chlorine atoms, plus alkyl-aromatic compounds as diluent (Fig. 4). This aromatic fraction was separated by distillation at pressure of 1 torr and the residual containing PCBs was used as substrate for experiments.

In a 250-mL three-necked round-bottomed flask, a mixture composed of solid iron(II)sulphate (0.29
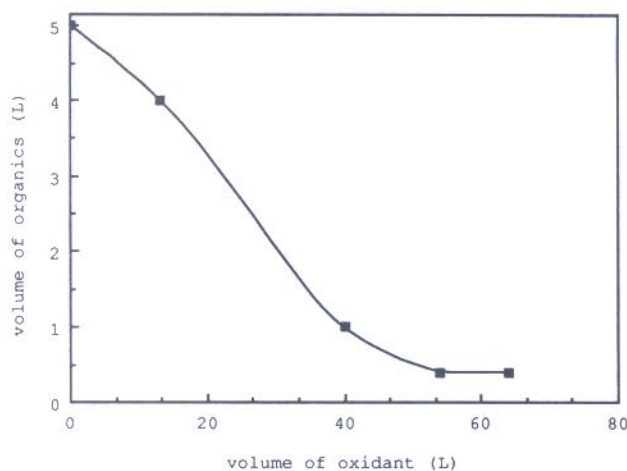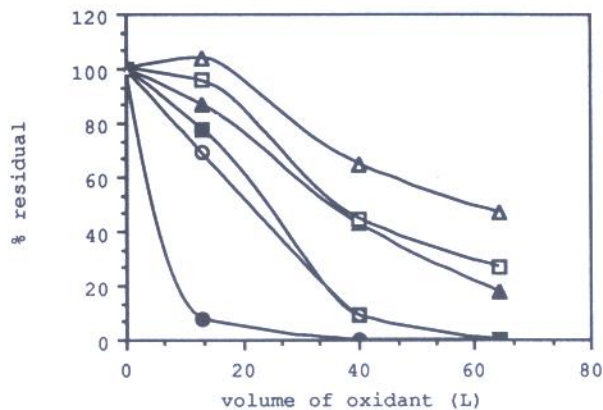

FIGURE 3. Degradation kinetics curves of ■ mesitilene, or TBP, ● TAA1, Kerosene: A (▲) − B (□) − C (△) by gaschromatographic data (method 1).
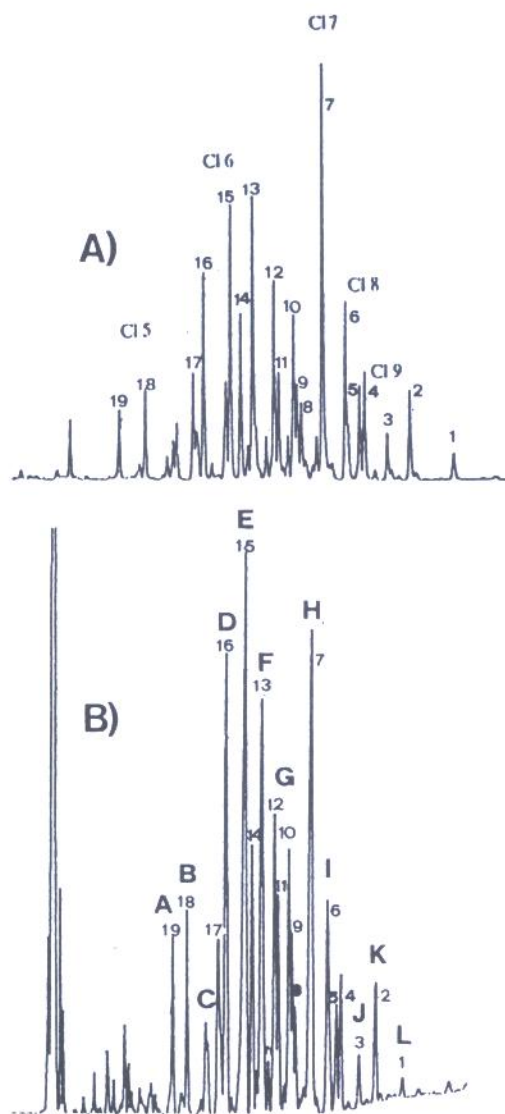

FIGURE 4. The eluation profiles of A) Aroclor 1260 (by reference 9) and B) Askarel oil (gaschromarographic method 2). The numbers indicate the peaks agreements.

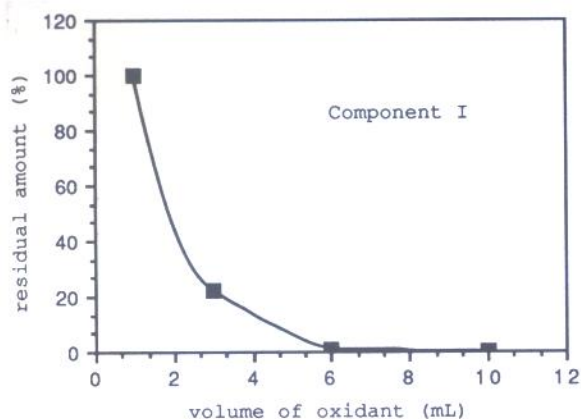**FIGURE 2.** Decrease of organic volume versus liters of oxidant.

FIGURE 5. WOX of PCBs in acetic acid. Kinetic curve of component I of Fig. 4.

mmol/mL) and substrate in appropriate organic solvent (5 mL) was heated at reflux temperature (about 100°C) under vigorous magnetic stirring. For the gas chromatographic (GC) analyses, 10 microliters of mixture were periodically removed. In biphasic systems the samples were removed from organic phase. Moreover, at the end of the reaction period, the remaining PCBs were extracted with 10 mL of CH₂Cl₂ and analysed by GC.

By preliminary tests carried out, by using n-dodecane acting both as solvent and as suitable internal standard for GC analysis (8), it was noted that WOX

carried out in heterogeneous media is ineffective. In subsequent experiments, it was found that the use of a cosolvent considerably improved the oxidation speed since the reaction takes place in a homogeneous phase. Figure 5 shows the typical pattern of decay curve common to all Askarel oil components by homogeneous WOX conducted in acetic acid as cosolvent. The PCBs concentration was 2.5 g/L and the oxidant solution (36% H_2O_2 plus concentrated H_2SO_4 (20 mL/L)) was added at a constant flow rate of 3.74 mL/h. The results indicate that PCBs oxidation carried out in this condition is enormously increased. In fact, in the final organic extract (CH_2Cl_2) only traces of the organic substrates (about 2% of the starting amount) are recovered. These results were not confirmed by subsequent test performed in the same conditions but with the 10 times higher starting substrate concentration. In this case, a separation between phases and the consequent segregation of PCBs in the organic layer occurred and, therefore, the reaction was ineffective. That can be avoided by using a cosolvent of substances which can react with water and remove it from the system. On this subject, in Fig. 6 there are the gas chromatograms of the starting PCBs solution (25 g/L) and the CH_2Cl_2 extract after the WOX in acetic anhydride. On the average, 95% of the initial PCBs were degraded, while performing at the same starting concentration but in acetic acid media, the final mixture
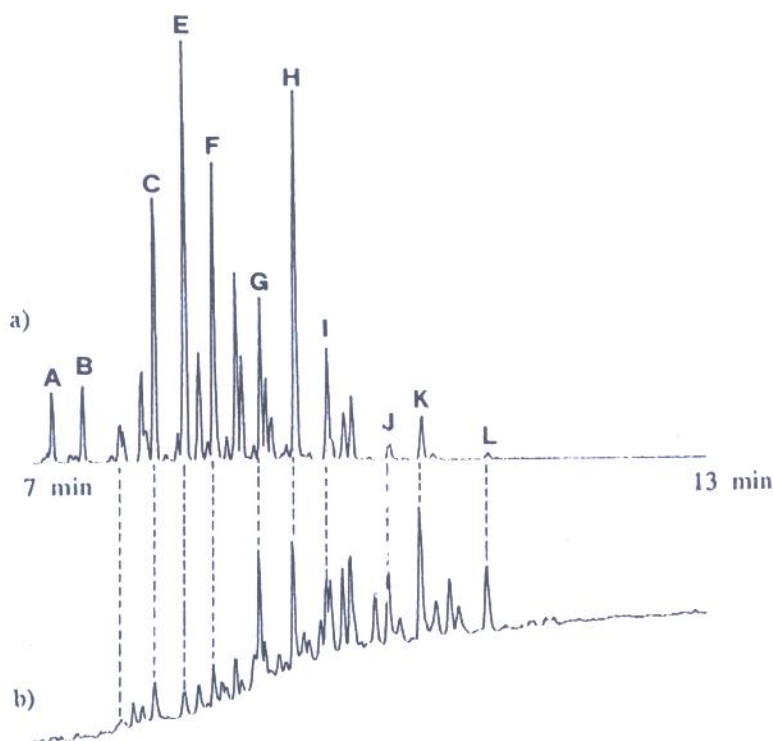

FIGURE 6. WOX of PCBs in acetic anhydride. The eluation profiles of a) the starting solution and of b) the methilenic extract after 11.35 mL of oxidant.

TABLE 1
Residual Amount of PCBs Congeners Labelled in Fig. 6

PCBs	Residual Amount (%)	PCBs	Residual Amount (%)
A	Traces	G	0.87
B	Traces	H	0.87
C	0.5	I	1.49
D	0.5	J	10.6
E	0.13	K	8.19
F	0.35	L	~24

contained 40% of these compounds. The residual percent of substrate components (peak A-L of Fig. 6), estimated with external standard method, are listed in Table 1. Their values vary from nearly zero to 24% (peak L); that indicates, as it could be expected, the more chlorinated congeners are also the most refractory to WOX.

Olive Vegetation Waters

The disposal of olive vegetation waters is, in olive-oil producing countries, one of the most difficult problems to solve because of 1) the amount of waste/water involved (up to 1 L/Kg); 2) the great dispersion of oil mills, generally small and working only few months per year; 3) the polluting properties (COD ~100 g/L, BOD ~50 g/L), owing to the presence of high amounts of organic matter, generally over 100 g/Kg (11). These waste waters have particularly poor biodegradability from the presence of both simple and polymeric phenols (12). Therefore, we have chosen the olive-vegetation waters as a model to verify the application of WOX to conventional and industrial wastes. The experiments were performed at 100°C with 36% H_2O_2 as oxidant, while the iron salts, already present in the starting samples, were used as a catalyst at the rate of about 100 mg/L. In several cases, the pH of polluting solution was adjusted with concentrated H_2SO_4. For COD analyses and for titrimetric quantitation of hydrogen peroxide, some milliliters were perodically removed.

Moreover, to determine the best reaction conditions we have operated in two different ways: A) the oxidant was continuously added to 100 mL of substrate; B) the oxidant and the substrate were together fed at different flow rates in the reactor.

In Table 2, the experimental conditions of the tests are summarized while Fig. 7 shows the relating kinetic curves. On this subject, the theoretical concentration of H_2O_2 was the difference between the total amount added to the solution and the quantity already reacted with the organic substrate.

By comparison of Fig. 7A and 7B, respectively, to EXP.1 and EXP.2, it is evident that pH of starting solution is an important parameter for the reaction effectiveness. The addition of H_2SO_4 produces a catalyzing effect and, above all, prevents a pH increase which promotes the alkaly catalyzed auto-decomposition of hydrogen peroxide to oxygen and water, an unavoidable reaction in wet oxidation processes which use metal salt catalysts (13,14). In fact, the same amount of oxidant is consumed during the two experiments but, in the first case, the final COD of solution is considerably higher than the second one. A cleaner improvement of process was also obtained operating in the same conditions of EXP.1 but by using method B (EXP.3). In this case, two important aims, at least during first times of reaction, were obtained: the organic matter concentration is substantially constant and the oxidant concentrations are always higher than by using method A. As shown in Fig. 7C, at the beginning, COD values decreased faster than previous tests, then remained essentially uniform as long as organics were fed and, finally, arrived at amounts nearly half of the first experiment. This demonstrates that the oxidation reaction was accelerated while simultaneously the auto-decomposition kinetic was unchanged.

The final experiments simultaneously increased the feeding of both the oxidant and the substrate, and have substantially confirmed previous results; particularly they have indicated that, in this way, the

TABLE 2
Experimental Conditions of WOX Tests on Olive Vegetation Waters

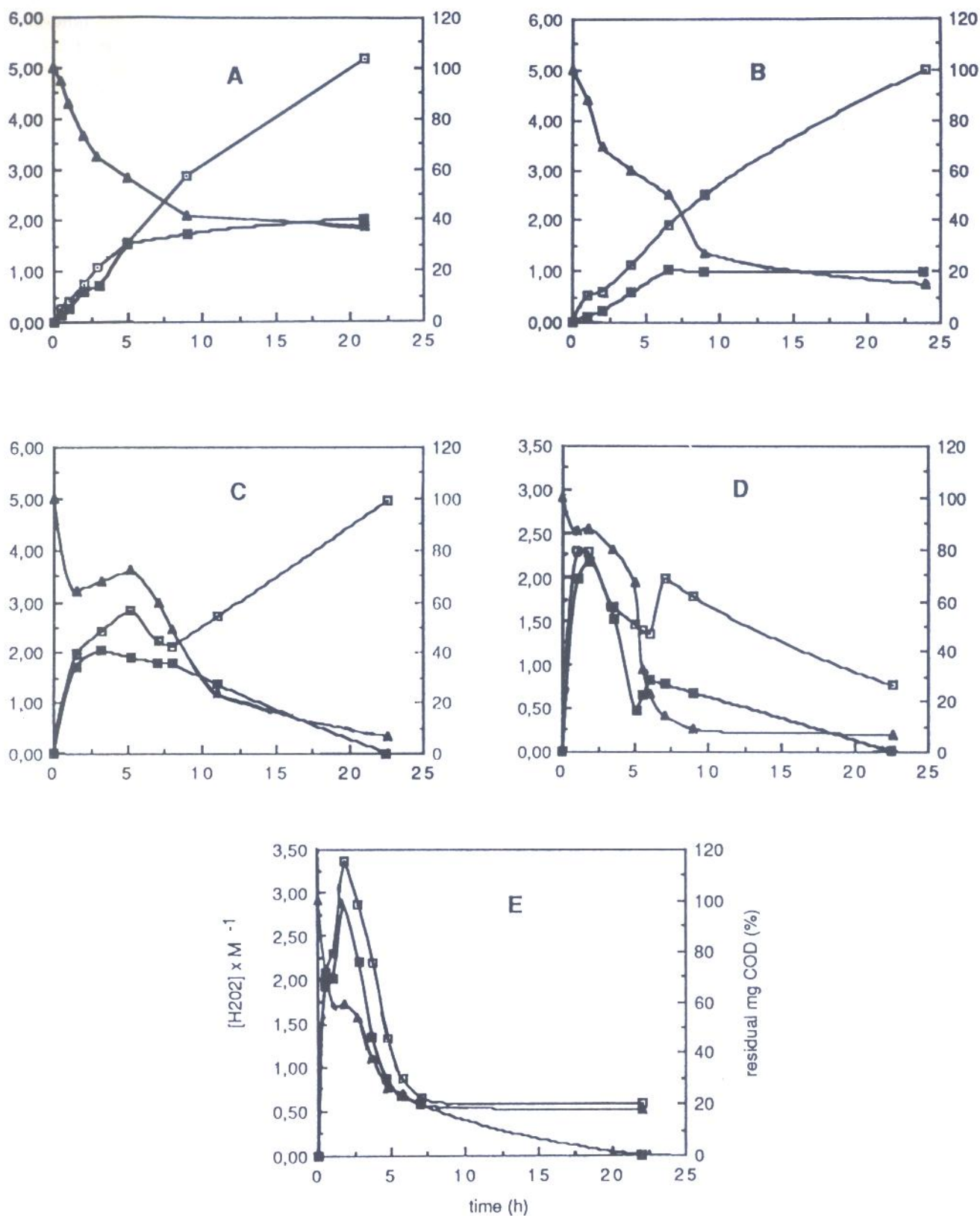| EXP	[H_2O_2]	H_2O_2 Flow Rate mL/h	Waste Waters Flow Rate mL/h	Initial pH	Final pH	Method
1	10.5 M	5.1	–	5.4	8.0	A
2		5.1	–	2.0	4.0	A
3		5.0	15.0	5.4	10	B
4		15.0	47.1	5.4	9.8	B: oxidant feeding was stopped after ~1.5 h; then it started again after 5 h.
5		17.0	89.0	2.0	3.2	B: oxidant feeding was stopped after 1.75 h and led until the reaction end.

FIGURE 7. Kinetic curves of tests 1–5 of Table 2: ▲ residual mg COD (%), □ theoretical [H₂O₂], ■ real [H₂O₂].

oxidation process can be further accelerated but the effectiveness does not improve. This could most likely be obtained by changing the flow rates ratio with the increases of H_2O_2. Finally, Table 3 summarizes the quantitative results of experiments: the values present in the fourth column regard the COD decrease owing to dilution for the oxidant addition, while the values present in the last two columns give a more evident idea of differences in reaction effectiveness and oxidant consumptions.

TABLE 3
Quantitative Results of Experiments Described in Table 2

	Initial COD (g/L)	Final COD (g/L)	Destroyed COD Percent[a]	Destroyed COD Percent[b]	g COD/ Mol H_2O_2	g H_2O_2/ g COD
EXP.1	118566	22446	81	63	13.3	2.56
EXP.2	105879	7529	93	85	15.7	2.17
EXP.3	130293	4480	97	93	17.1	1.99
EXP.4	107165	5453	95	93	15.0	2.27
EXP.5	107821	13648	87	82	15.3	2.22

[a]values calculated by $[(COD_i - COD_f)/COD_i] \times 100$;
[b]values calculated by $[(COD_i \cdot V_i - COD_f \cdot V_f)/COD_f \cdot V_f] \times 100$, where COD_i and V_i are the initial values of respectively COD and Volume and COD_f and V_f are the final values.

Atrazine

Experiments on aqueous solution containing small amounts of atrazine, as *s*-triazine herbicides model, was performed by using the pilot plant shown in Fig. 8. In this case, as a catalyst U.V. light emitted by four lamps at mercury low pressure with a maximum emission of 254 nm were used.

The oxidant and wastes (25 L) are continuously fed into an U.V. reactor at room temperature through pumps and are drawn off into the water drum so as to form a recycling system. 25 mL samples are periodically removed for HPLC and TOC analyses. Figure 9 shows the results obtained by feeding 20 mg/L atrazine solutions at flow rate of about 400 L/h and using as oxidant hydrogen peroxide at a different concentration and flow rate. An initial con-

trol test was carried out at U.V. lights turned off and without H_2O_2 feeding. Three different reaction conditions were used: a) no H_2O_2 feeding and U.V. light on; b) oxidant concentration of 0.420 M at flow rate of 4.76 mL/min; c) oxidant concentrations of 10.5 M at flow rate of 13.2 mL/min. It is evident, from results, that the atrazine oxidation occurs substantially with a two-step mechanism. Initially, decomposition by photolysis and hydroxytriazines, are probably the major photoproducts (15,16). This first process doesn't depend on H_2O_2 feed. In fact, kinetic curves b, c, of Fig. 9 are exactly in agreement with data of experiment a, carried out without oxidant adding. Hydrogen peroxide acts only in following this step and, in preference, on photoproducts. At small concentrations of oxidant (EXP.b), the WOX is
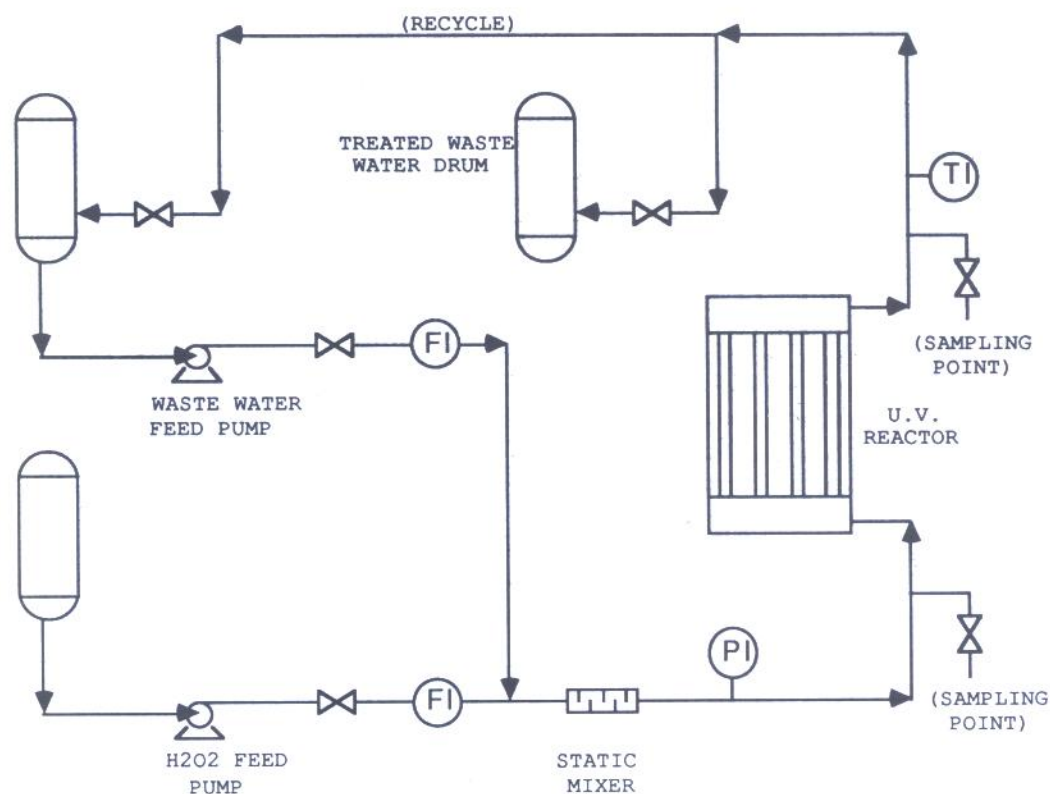

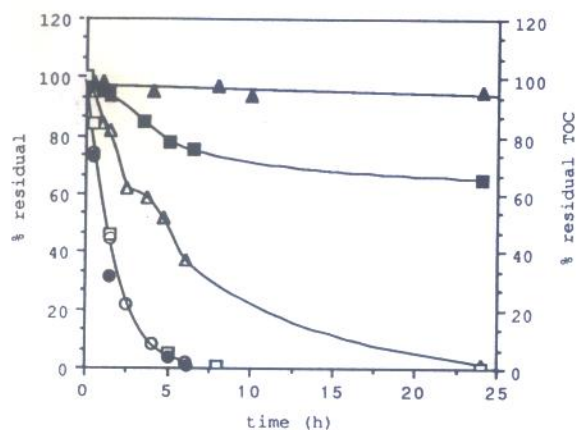**FIGURE 8.** Pilot plant for WOX experiments with U.V. light as catalyst.

FIGURE 9. WOX of atrazine. Kinetic curves of tests a) □, b) ●, c) ○ and of the control test (▲). TOC analyses of ■ exp.b and △ exp.c.

highly ineffective and final products of this reaction are intermediates. On the contrary, the atrazine degradation is complete starting by concentrated hydrogen peroxide. In this case, both reactions, photodegradation and oxidation, take place simul-
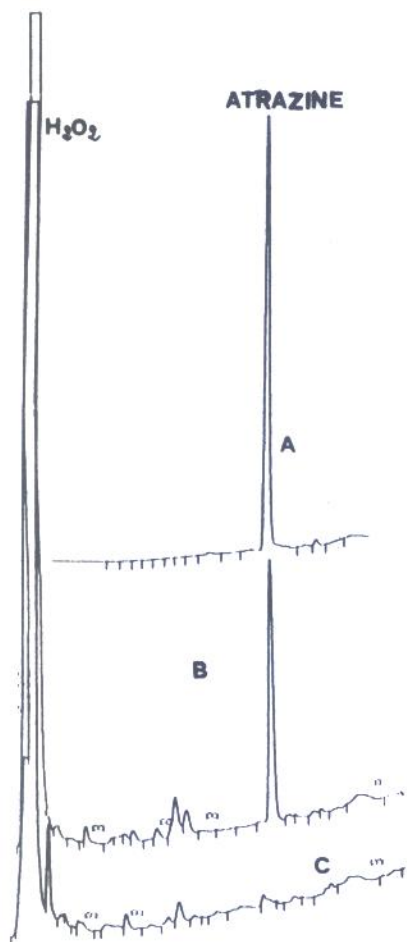
taneously so intermediates don't increase during the process, as shown in Fig. 10. This is also confirmed by TOC analyses shown in Fig. 9. In order to apply the WOX process to the detoxification of pesticide-polluted drinking water, further experiments should be performed to minimize oxidant consumptions. On this subject, a most important parameter is the exposure time of oxidant to U.V. light and, of course, the feeding flow rate of reagents.

CONCLUSIONS

The studies performed at a temperature up to boiling point have demonstrated the efficiency of WOX for the treatment of the radioactive wastes and toxic organic pollutants. The results of preliminary pilote-scale tests on radioactive solvent wastes have substantially confirmed the laboratory data (8). In the case of conventional waste water treatment, the high cost of hydrogen peroxide and the necessity to reduce drastically the COD and BOD values of the wastes, because of the severity of the disposal regulations, suggests to develop the WOX at relative high temperature. On this subject, we are building a pilot plant to treat waste waters at a temperature of about 200°C and a pressure up to 20 bars. Moreover, in the same pilot plant, the possibility to carry out a preliminary oxidation with pure oxygen and to utilize, as catalysts, both U.V. light and metallic salts has been foreseen.

FIGURE 10. WOX of atrazine. HPLC chromatograms of initial solution (a), after 1.5 h (b) and after 5 h of reaction (c).

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