Partial degradation of five pesticides and an industrial pollutant by ozonation in a pilot-plant scale reactor

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Abstract

Aqueous solutions of a mixture of several pesticides (alachlor, atrazine, chlorfenvinphos, diuron and isoproturon), considered PS (priority substances) by the European Commission, and an intermediate product of the pharmaceutical industry (α-methylphenylglycine, MPG) chosen as a model industrial pollutant, have been degraded at pilot-plant scale using ozonation. This study is part of a large research project [CADOX Project, A Coupled Advanced Oxidation-Biological Process for Recycling of Industrial Wastewater Containing Persistent Organic Contaminants, Contract No.: EVK1-CT-2002-00122, European Commission, http://www.psa.es/webeng/projects/cadox/index.html [1]] founded by the European Union that inquires into the potential coupling between chemical and biological oxidations for the removal of toxic or non-biodegradable contaminants from water. The evolution of pollutant concentration, TOC mineralization, generation of inorganic species and consumption of O_3 have been followed in order to visualize the chemical treatment effectiveness. Although complete mineralization is hard to accomplish, and large amounts of the oxidant are required to lower the organic content of the solutions, the possibility of ozonation cannot be ruled out if partial degradation is the final goal wanted. In this sense, Zahn–Wellens biodegradability tests of the ozonated MPG solutions have been performed, and the possibility of a further coupling with a secondary biological treatment for complete organic removal is envisaged.
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1. Introduction

Directive 2000/60/EC establishes a new framework for a water pollution strategy that includes a list of 33 priority substances (PS), that represent a significant risk to the European aquatic environment [2]. Several water-soluble pesticides are included among these substances: alachlor, atrazine, chlorfenvinphos, diuron and isoproturon (of special interest because of their mobility in the environment and their presence in surface and groundwater). The processes and technologies available at the present time for the treatment of polluted water are diverse [3,4]. The wastewater treatment techniques most frequently used can be divided into physical, biological and chemical. Urban wastewater is usually only treated with physical and biological

techniques that reduce the pollution, but these are not enough to comply with standards that are becoming stricter. The general tendency is toward the use of more chemical treatments, both to comply with standards and to recycle used water. Moreover, wastewater containing pesticides cannot very often be treated by biological techniques, since they are toxic for the microorganisms and therefore their biodegradation is not possible.

This work presents data concerning the ozonation of the mixture of the five above mentioned pesticides and α-methylphenylglycine (MPG, a by-product of the pharmaceutical industry and typically non-biodegradable compound). The use of ozone as an oxidant for drinking water treatment and disinfection is well established [5,6]. The mechanisms and the rates of attack of ozone to organic compounds in different experimental conditions have been clarified by Hoigné and Bader [7]. Fewer are the real applications of ozone for the treatment of real wastewaters, because the removal of high concentrations of pollutants always implies the use of large amounts of

ozone, making difficult the economical implementation of the technique. Nevertheless, reviews can be found in the scientific literature concerning such a topic [8]. Taking into account that the final goal of the CADOX project was the partial degradation of the pollutants in a first chemical treatment, a moderate use of chemical oxidants would be expected. In such circumstances, ozone cannot be rejected as a viable oxidant, and the present study was aimed at collecting data from a pilot-plant scale reactor where the partial ozonation of the pesticides and MPG was carried out.

The lab-scale ozonation of the five different pesticides studied has been previously reported by other authors. In the case of alachlor the 2nd order kinetic constant of reaction between alachlor and ozone was found to be $k = 3.8\,\mathrm{M^{-1}\,s^{-1}}$ [9], while $t_{1/2} > 2.4\,\mathrm{h}$ at the experimental conditions reported (pH 7). TOC removal by means of dark ozonation of alachlor is slow (20% in 1 h [10]), and complete mineralization was not reported. The 2nd order kinetic constant of reaction between atrazine and ozone at pH 7 is $k = 6.0\,\mathrm{M^{-1}\,s^{-1}}$, as reported by other authors [11], and the mineralization of atrazine by ozone hardly occurs due to the stability of some reaction intermediates. It is known that, at pH 2, atrazine is degraded to cyanuric acid, a compound that is resistant even to the hydroxyl radical attack. In a study about the disinfection of water containing low levels of pesticides [12] chlorfenvinphos was poorly degraded by ozonation. At pH 8.3 and 20 °C, with O_3/TOC dosages of 0.95, the percentage of pesticide eliminated from a 6.4 µg L^{-1} solution was 70%. No data was given about the mineralization of the pesticide. In the same work the ozonation of diuron was studied, and 98% elimination was reported for a 6.4 µg L^{-1} solution at pH 8.3, 20 °C and with a O_3/TOC dosage of 0.95. Again, no data is shown about the mineralization of this pesticide. Finally, for a 10 mg L^{-1} solution of isoproturon, an effective 99% removal in 5–15 min and a 2nd order kinetic constant of reaction $k = 141\,\mathrm{M^{-1}\,s^{-1}}$ have been reported [13]. It has been also found [14] that the initial fast isoproturon degradation is followed by slower primary by-products degradation. Final breakdown of the aromatic structures and formation of low molecular weight organic acids has been proven, being formic, acetic, and oxalic acid, in the µg L^{-1} range of concentration, the final and persistent products in solution.

All these previous works seem to point toward a rather quick destruction of the original pesticides when treated with ozone, but with a slower removal of the reaction intermediates that, in some cases, cannot be totally degraded. This might not be a drawback if ozonation is designed as a previous step to be used before a secondary treatment like, for example, a biological one. In such case the chemical oxidation with ozone would be suitable if reaction intermediates are not destroyed but have biodegradable natures. Thus, it seems interesting to study the ozonation of the five pesticides at pilot-plant scale just to follow the course of the reaction, especially when the pesticides are treated together. That would give a first insight into the possible coupling between ozonation and a secondary treatment.

Pollutants disappearance, TOC removal, formation of inorganic species like Cl$^-$, NH$_4^+$, NO$_3^-$ or PO$_4^{3-}$, and ozone consumption were quantified. In the case of MPG biodegradability tests pointing toward the generation of biodegradable ozonation intermediates were performed.

2. Experimental

2.1. Chemicals

The pesticides used in this study were, alachlor (95%, C$_{14}$H$_{20}$ClNO$_2$, Aragonesas Agro S.A. technical grade), atrazine (95%, C$_8$H$_{14}$ClN$_5$, Ciba-Geigy technical grade), chlorfenvinphos (93.2%, C$_{12}$H$_{14}$Cl$_3$O$_4$P, Aragonesas Agro S.A. technical grade), diuron (98.5%, C$_9$H$_{10}$Cl$_2$N$_2$O, Aragonesas Agro S.A. technical grade), isoproturon (98%, C$_{12}$H$_{18}$N$_2$O, Aragonesas Agro S.A. technical grade). α-Methylphenylglycine (MPG, C$_9$H$_{11}$NO$_2$) was supplied by Deretil Co. Fig. 1 shows the chemical compounds structure.

The water used to prepare the pesticides and MPG solutions was distilled water (conductivity <10 µS cm^{-1}, [Cl$^-$] = 0.2–0.3 mg L^{-1}, [SO$_4^{2-}$] = 0.2–0.3 mg L^{-1}, organic carbon <0.5 mg L^{-1}). One of the MPG experiments was carried out mixed with real wastewater obtained from a DERETIL
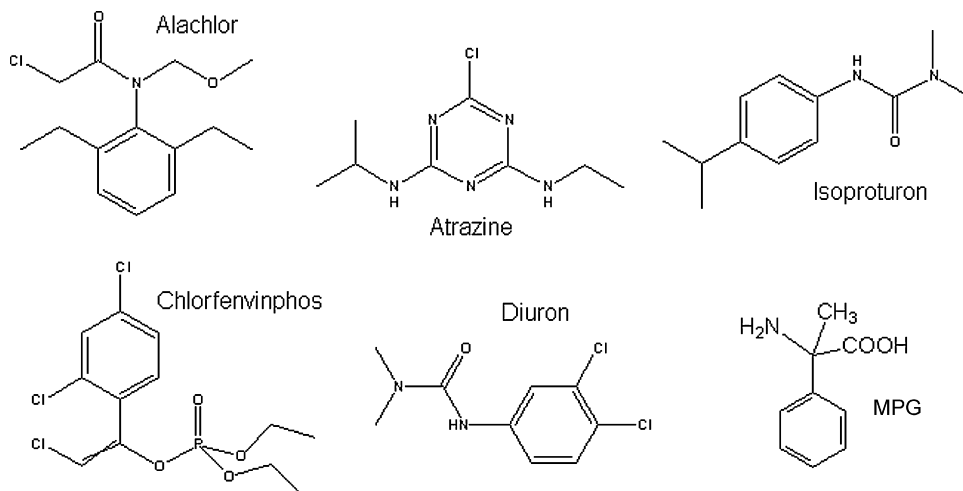

Fig. 1. Chemical structure of the six compounds studied in the present work.

wastewater treatment plant effluent (*Real WW* in the figure legends). Since the industrial production is carried out using sea water as process water, the ion composition of such industrial effluent is close to the typical composition of sea water: NaCl, $28 \, g \, L^{-1}$; MgCl$_2$, $4.8 \, g \, L^{-1}$; MgSO$_4$, $3.5 \, g \, L^{-1}$; CaCl$_2$, $1.6 \, g \, L^{-1}$; KCl, $0.8 \, g \, L^{-1}$; NaHCO$_3$, $0.1 \, g \, L^{-1}$; NO$_3^-$, 200–$600 \, mg \, L^{-1}$; NH$_4^+$, 0–$40 \, mg \, L^{-1}$; NO$_2^-$, 0–$20 \, mg \, L^{-1}$; total P, 1–$5 \, mg \, L^{-1}$. Other characteristics vary as a function of the process: COD, 200–$400 \, mg \, L^{-1}$; TOC, 100–$200 \, mg \, L^{-1}$; and suspended solids, 20–$100 \, mg \, L^{-1}$.

Due to the different characteristics (mainly water solubility) of the different compounds, the preparation of the pesticide solutions was done by adding the pure compound to water and mixing during several hours in the laboratory in two 5-L flasks (i.e., 10 L) at 60 °C. Afterwards, the solution was diluted with more water, up to a total volume of 50 L, and transferred to the ozone reactor, where the final temperature achieved was 30 °C. The initial concentration of the pesticides in the mixture was: $16.6 \, mg \, L^{-1}$ of atrazine; $20.1 \, mg \, L^{-1}$ of alachlor; $16.9 \, mg \, L^{-1}$ of diuron; $18.1 \, mg \, L^{-1}$ of isoproturon; $18.1 \, mg \, L^{-1}$ of chlorfenvinphos. In the case of MPG all the experiments were performed at $500 \, mg \, L^{-1}$, and due to its high solubility, the compound was directly added to the water contained in the ozone reactor. No pH adjustment was done.

2.2. Ozone reactor

The ozonation reactor consists of an ozone generator (TRAILIGAZ Labo 5 LOX, maximum ozone production of $20 \, g \, h^{-1}$ at 11.7%, w/w), an ozone analyser (BMT 964), an oxygen cylinder for oxygen supply, a contact column (1800 mm high water column, 50.1 L maximum capacity, with the flow inlet on the top), and an ozone destructor (supplied by TRAILIGAZ). Piping and valves are made of polypropylene (for water flow) and PTFE (for ozone flow), and the contact column is made of PVC (opaque in the base of column (192 mm internal diameter) and transparent in the top of column (152 mm internal diameter)). The power of the ozone generator and the oxygen flow were set in all the tests at 55 W (or 120 W in one experiment) and $200 \, L \, h^{-1}$, respectively, ensuring a constant supply of O$_3$ to the contact column. Residual ozone has been measured at the outlet of the contact column during all the tests.

2.3. Chemical analysis

The mineralization degree of the chemicals studied was followed by measuring the total organic carbon (TOC) by direct injection of the filtered samples into a Shimadzu-5050A TOC analyzer provided with a NDIR detector and calibrated with standard solutions of hydrogen potassium phthalate. All compounds were analysed using reverse-phase liquid chromatography (flow $0.5 \, mL \, min^{-1}$) with an UV detector in a HPLC-UV Chromatograph (Agilent, series 1100) and a C-18 column (LUNA 5 μm, 3 mm × 150 mm from Phenomenex). The pesticides mixture was analysed by a step gradient programme with water acetonitrile as mobile-phase. The ratios H$_2$O/CAN applied were $0'$–$12'$: 65/35 and $12.1'$–$25'$: 35/65. A 50 mM phosphoric acid

solution adjusted to pH 2.5 with NaOH was used for MPG analysis. Cation concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm × 250 mm column. Isocratic elution was done with H$_2$SO$_4$ (20 mN) at a flow rate of $1.2 \, mL \, min^{-1}$. Anion concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. Flow rate was $1.5 \, mL \, min^{-1}$ and elution was done with NaOH gradient programmes. The Zahn–Wellens test corresponding to the MPG solutions pre-treated by ozonation were carried out under conditions close to those of a conventional municipal wastewater treatment plant. Activated sludge coming from a wastewater treatment plant operating with sea water was used to prepare the $0.2 \, g \, L^{-1}$ of TSS (total suspended solids) required in the test specifications [15].

3. Results and discussion

The first question, and very important one, to be addressed was the suitable ozonator dimensions to be used. Since previous lab-scale experiments had shown that the reaction rate of ozonation of MPG was faster than any of the reactions between ozone and the five pesticides, it was assumed that the larger consumption of ozone was taken place with MPG and, thus, the capacity of the ozone generator had to be fixed taken into account the reaction with such chemical. The preliminary experiments with MPG solutions of $500 \, mg \, L^{-1}$ gave an initial (and maximum) O$_3$ consumption around 16 g per g of TOC degraded, and a maximum removal rate of $8 \, mg \, L^{-1} \, h^{-1}$ of TOC. Taking into account the treatment of a 50 L solution, the requirement for ozone production was $6.4 \, g \, h^{-1}$. Considering an ozone transfer around 50%, $12.8 \, g \, O_3 \, h^{-1}$ had to be supplied. For applications like disinfection where the amount of contaminants is low and the effluent flow is high, dry air can be used as ozone source since it is cheap, and concentrations from 20 to $50 \, g \, O_3 \, Nm^{-3}$ are easily obtained. In the present case (elimination of important amounts of organic matter from a wastewater) larger amounts of ozone are needed. Because the concentration of contaminant is high and the flow of polluted water low, dry oxygen is the best choice, since concentrations between 100 and $200 \, g \, O_3 \, Nm^{-3}$ can be obtained at reasonable prices. Thus, the ozonator used in these experiments was able to produce $12.8 \, g \, O_3 \, h^{-1}$ at an ozone concentration of 11.7% (w/w) in pure oxygen. Because the oxidation kinetics is low the ozone transfer was poor and a large fraction of ozone was lost in the off gas.

Fig. 2 shows the time-course of the different pesticides concentration during the ozonation of their aqueous mixture. As can be seen, all the pesticides are completely degraded although there are large differences in removal rates among them, being isoproturon completely removed in 30 min while 270 min are needed for alachlor complete disappearance. The reactivity with ozone seems to follow the order: isoproturon > diuron > atrazine > chlorfenvinphos > alachlor. This behaviour agrees with the reaction rates previously reported by other authors (see Section 1). Nevertheless, the removal of TOC is a quite different matter. Fig. 3 shows the evolution of TOC during the reaction. As can be seen, after more than 1000 min
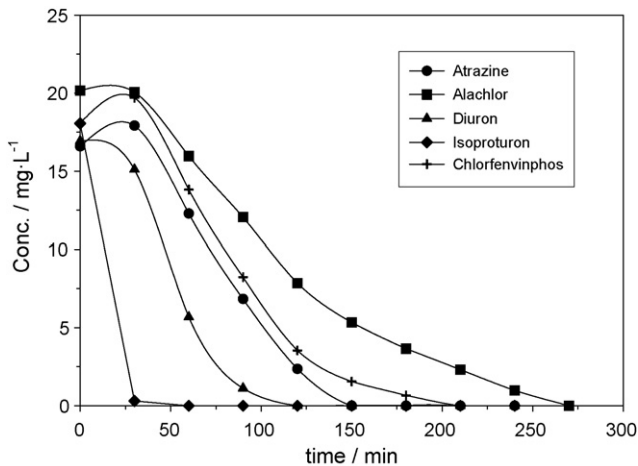
Fig. 2. Time-course of the concentration of the five pesticides (atrazine, alachlor, diuron, isoproturon and chlorphenvinfos) during the ozonation of their aqueous mixture. Aqueous volume = 50.1 L, O_2 flow = 200 L h^{-1}, $[O_3]_{gas-phase}$ = 26.8 g m^{-3}, unbuffered solution.

the TOC is just 47.9 mg L^{-1} (initial TOC of the solution was 64.8 mg L^{-1}), thus, only 26% of the initial TOC is removed. It is clear that ozonation is not a good method for the total mineralization of the organic load of waters containing those pesticides, nevertheless it is not a serious drawback since the goal of the present research was to study the potential of ozonation for a partial degradation of them. Fig. 3 also contains data concerning some of the inorganic ions formed during the reaction. Since the original pesticides contain heteroatoms like Cl, N or P, formation of Cl$^-$, NH$_4^+$, PO$_4^{3-}$ or NO$_3^-$ is expected during the reaction. Taking into account the initial concentration of each pesticide and considering complete mineralization, the maximum stoichiometric concentrations of each atom expected in solution are: 26.9 mg Cl L^{-1}, 13.3 mg N L^{-1}, and 3.85 mg P L^{-1}. In the case of Cl$^-$ the final amount detected is 20 mg L^{-1}, i.e., 74.3% of the maximum expected concentration at total mineralization. Since TOC removal was only 26%, it is clear that Cl is eliminated from the organic matter in the first steps of reaction, leaving non-halogenated organic intermediates in solution. For N species the
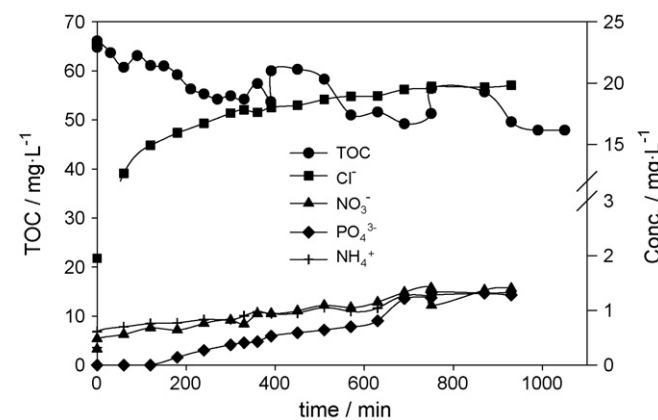
final concentrations after 900 min of reactions are 1.40 mg L^{-1} (NO$_3^-$) and 1.33 mg L^{-1} (NH$_4^+$), i.e., 1.35 mg N L^{-1}, or the 10.1% of the maximum expected N in solution. This figure seems to be in contradiction with the fact that 26% TOC removal takes place at the same time, because mineralization implies the release of inorganic N and, consequently, at least 26% of the maximum expected N concentration should had been detected. Most probably, formation of other species like NO$_x$ is responsible for the detected unbalance. Concerning the presence of P as PO$_4^{3-}$, 1.28 mg L^{-1} (0.42 mg L^{-1} of P) are detected, i.e., 13.5% of the expected P at complete mineralization. From the data reported it seems plausible to conclude that Cl atoms are released during the first steps of pesticide degradation while N and P are only released at the final steps of the ozonation.

Concerning the consumption of ozone during the reaction, Fig. 4 displays the amount of ozone lost (exiting the reactor), and the ozone consumed, both, per m^3 of gas-phase, and in total. When examining the data it has to be remembered that the ozone entering the reactor was constant and equal to 26.8 g m^{-3}. As can be seen, the mass transfer is rather poor because even at the beginning of the ozonation, when no ozone is in aqueous solution and the reaction rate is faster, requiring the highest consumptions of the oxidant, approximately 17 g m^{-3} of ozone are lost at the exit of the reactor, and no more than 10 g m^{-3} react in solution. From there the mass transfer worsen, being close to zero at the end of the reaction. The total amount of ozone consumed through the course of the reaction was 7.8 g (with a ratio of 9.2 g O$_3$ consumed per g TOC degraded) far from the 93.8 g produced by the ozonator during the 1050 min of reaction. The decay of ozone consumption with time indicates that even the design of a more efficient mass transfer device for the injection of ozone in solution would no represent a dramatic change on reaction rate.

Therefore, the mixture of pesticides was treated with ozone obtaining a rather discrete removal of TOC and consuming large amounts of ozone. Parent compounds were removed from solution after long ozonation time and total dechlorination was hardly achieved. This means that biodegradability can be attained only after high ozonation times, involving an elevated

Fig. 3. Time-course of the TOC, Cl$^-$, NO$_3^-$, PO$_4^{3-}$ and NH$_4^+$ concentrations during the ozonation of the pesticides mixture. Aqueous volume = 50.1 L, O$_2$ flow = 200 L h^{-1}, $[O_3]_{gas-phase}$ = 26.8 g m^{-3}, unbuffered solution.
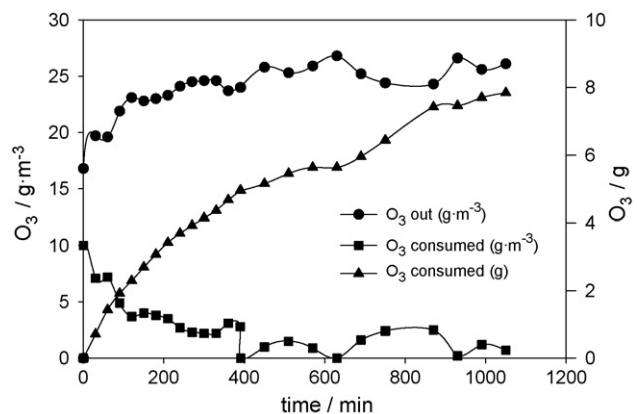

Fig. 4. Time-course of the ozone consumption (in terms of gas-phase concentration of ozone and total mass of ozone) and ozone leaving the reactor (in terms of gas-phase concentration) during the ozonation of the pesticides mixture. Aqueous volume = 50.1 L, O$_2$ flow = 200 L h^{-1}, $[O_3]_{gas-phase}$ = 26.8 g m^{-3}, unbuffered solution.
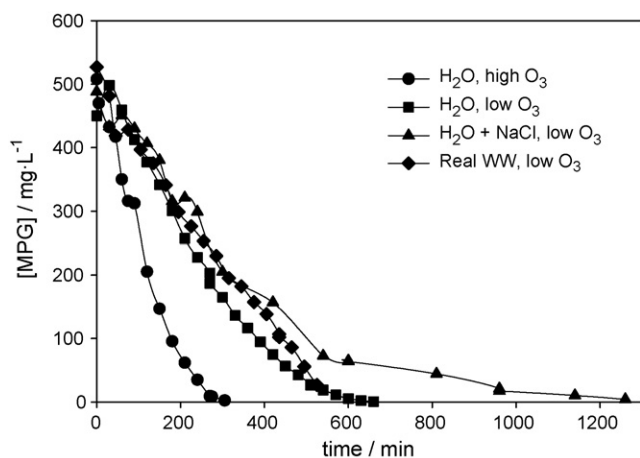
Fig. 5. Time-course of MPG concentration during the ozonation of different aqueous solutions: (a) distilled H_2O, high dose ($47.7 \, g \, m^{-3}$) of O_3; (b) distilled H_2O, low dose ($21.9 \, g \, m^{-3}$) of O_3; (c) distilled $H_2O + 35 \, g \, L^{-1}$ of NaCl, low dose ($21.9 \, g \, m^{-3}$) of O_3; (d) real wastewater (see Section 2), low dose ($21.9 \, g \, m^{-3}$) of O_3. Aqueous volume = 50.1 L, O_2 flow = $200 \, L \, h^{-1}$, unbuffered solution.

Fig. 6. Time-course of TOC during the ozonation of different aqueous solutions of MPG: (a) distilled H_2O, high dose ($47.7 \, g \, m^{-3}$) of O_3; (b) distilled H_2O, low dose ($21.9 \, g \, m^{-3}$) of O_3; (c) distilled $H_2O + 35 \, g \, l^{-1}$ of NaCl, low dose ($21.9 \, g \, m^{-3}$) of O_3; (d) real wastewater (see Section 2), low dose ($21.9 \, g \, m^{-3}$) of O_3. Aqueous volume = 50.1 L, O_2 flow = $200 \, L \, h^{-1}$, unbuffered solution.

electricity consumption and environmental impacts. Partial mineralization of the solution for a potential secondary treatment in a biological reactor does not seem a viable alternative for the treatment of the pesticides mixture.

The other part of the present research concerns the ozonation of MPG solutions. No previous data of MPG ozonation has been found in the literature. Fig. 5 shows the time-course of MPG during four experiments of ozonation. Two different gas-phase O_3 concentrations were tested, along with three different types of MPG containing waters: distilled water, distilled water in presence of $35 \, g \, L^{-1}$ of NaCl, and a real wastewater containing MPG and produced in a pharmaceutical industry (see the approximate composition of such water in Section 2). The data clearly indicates that important differences exist when the two different ozone concentrations (47.7 and $21.9 \, g \, m^{-3}$) are compared. As expected, a larger ozone concentration produces a faster MPG removal (around 400 min of difference between the two experiments for complete disappearance of MPG). If compared to the ozonation of the pesticides, the corresponding to MPG is faster, except for the case of isoproturon. However, similar MPG removal is noticed when the compound is present in the three different water solutions. The presence of large concentrations of NaCl or other inorganic salts have no a remarkable effect on the ozonation, except for the existence of a slow complete removal (see the long tail of the curve in Fig. 5) of the organic compound from the solution that contains $35 \, g \, L^{-1}$ of NaCl. This is not surprising since it is well known [16] that Cl^- is not a good scavenger of ozone at neutral pH (the reaction rate between Cl^- and ozone can hardly be measured). Something different would have been expected for the same reaction in a basic media, because the fast decomposition of ozone in such conditions produces $HO^\bullet$ that efficiently react with Cl^- [17]. In any case, the use of seawater in the industrial process is not a drawback for ozonation.

Something similar is observed in Fig. 6 where the evolution of TOC along the same reactions is presented. The largest TOC
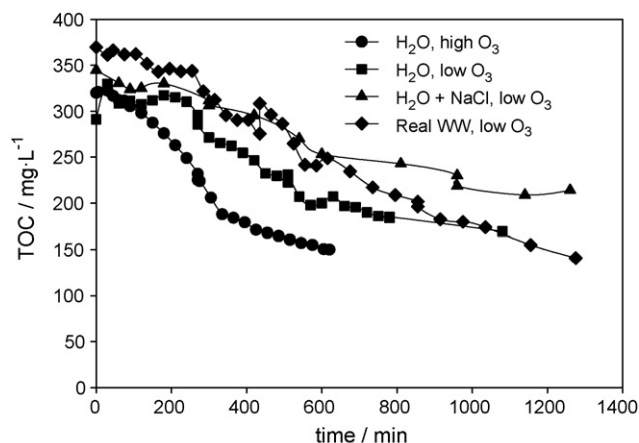
removal is obtained with the highest dose of ozone ($47.7 \, g \, m^{-3}$), but even in those conditions only 50% of the initial TOC disappears from solution, being clear than a decrease of TOC below 150 ppm would need long reaction times and large ozone consumptions. The behaviour of TOC in the three experiments carried out with $21.9 \, g \, m^{-3}$ of ozone is quite similar, the only important differences associated to the fact that the initial TOC was not exactly the same in the three experiments, and a visible difficulty for TOC removal at long reaction times with the solution containing $35 \, g \, L^{-1}$ of NaCl. For TOC decrease close to 50% reaction times longer than 1000 min are required. Like in the case of the pesticides the achievement of total mineralization seems a difficult goal with ozonation but this is not a dramatic inconvenience when only partial degradation of the initial organic load is pursued.

Because the only heteroatom present in the chemical structure of MPG is N, detection of NO_3^- and NH_4^+ at different reaction times was carried out during ozonation of MPG in distilled water with both 47.7 and $21.9 \, g \, m^{-3}$ of ozone. Fig. 7 contains the data that clearly shows that NH_4^+ is the main form of inorganic N in solution. Assuming an initial MPG solution of $500 \, mg \, L^{-1}$, complete mineralization, and exclusive formation of NH_4^+, a concentration of $58 \, mg \, L^{-1}$ of NH_4^+ should be expected. Thus, the $32.6 \, mg \, L^{-1}$ of NH_4^+ detected at the end of the reaction with the highest ozone dose is around 50% of the total expected N (the minor contribution of NO_3^- is not considered), matching the approximate 50% TOC removal detected in such circumstances. It seems reasonable to state that the evolution of the two parameters along time is similar, indicating a probable release of N at the last steps of mineralization. The oxidation of NH_4^+ to NO_3^- is more difficult, at least at the pH of the experiments.

Finally, the ozone consumed and the ozone leaving the reactor was measured in all the experiments with MPG. In general, the qualitative behaviour is the same in both cases. Thus, data concerning the ozone involvement in one of them (the ozonation of MPG dissolved in distilled water with a gas-phase ozone concentration of $47.7 \, g \, m^{-3}$) is shown in Fig. 8. The results are
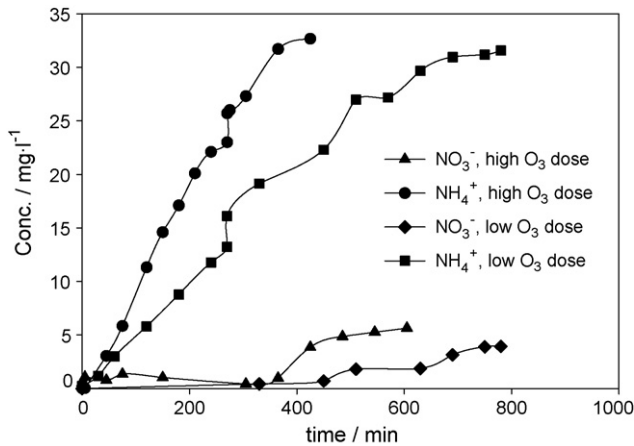
Fig. 7. Time-course of NO_3^- and NH_4^+ concentrations during the ozonation of different aqueous solutions of MPG: (a) distilled H_2O, high dose (47.7 g m^{-3}) of O_3; (b) distilled H_2O, low dose (21.9 g m^{-3}) of O_3. Aqueous volume = 50.1 L, O_2 flow = 200 L h^{-1}, unbuffered solution.

also similar to the situation observed during the ozonation of the pesticides mixture: a clear decrease of the consumed ozone (in terms of concentration) with time, meanwhile an increase of the concentration of ozone wasted was detected at the reactor outlet. Nevertheless, two aspects of the data deserve a more detailed comment. First, the amount of ozone initially consumed is high. In fact, at the beginning of the reaction, all the ozone entering the reactor is consumed. That can be due to the fast reaction between MPG and ozone. On the other hand, the concentration of ozone consumed changes very little in a period of time that goes from 50 to 300 min, and then decreases rapidly. The time required to eliminate the original compound (see Fig. 5) is approximately the same, indicating that the ozone consumed and leaving the reactor is stable as long as MPG is present in solution. Again, the fast ozonation of this compound can explain the situation. Once MPG is gone, and taking into account a slower reaction with the remaining organic intermediates, the consumption of ozone declines. The total amount of ozone consumed through

the course of the reaction was 40.9 g, 41.5% of the 98.6 g produced by the ozonator during the 620 min of reaction, with a ratio of 4.8 g O_3 consumed per g TOC degraded. The ratios corresponding to the rest of the MPG experiments (g O_3 consumed per g TOC degraded) were: 3.5 (distilled water + low O_3 dose), 5.1 (distilled water and 35 g L^{-1} NaCl), and 2.6 (real WW). In those cases the obtained data is not enough to disregard the need of a better mass transfer device for the injection of ozone in solution that could render appreciable changes on reaction rate.

Like in the case of the pesticides mixture, MPG was treated with ozone obtaining a rather discrete removal of TOC and consuming large amounts of ozone. Nevertheless, since partial mineralization of the solutions for a potential secondary treatment in a biological reactor was the goal, the experiments in the pilot-plant leave open the possibility of such a coupling between chemical and biological treatments. In the case of MPG dissolved in real wastewater, the Zahn–Wellens biodegradability test of the samples generated after ozonation at different times were carried out. MPG is a non-biodegradable compound, and the Zahn–Wellens test of the original solution of MPG gave no appreciable TOC removal after 28 days. Therefore, all samples used in the test were taken after the complete disappearance of the parent compound (555 min of reaction, 242 ppm of TOC remaining in solution). Fig. 9 shows the data corresponding to those tests along with the line of 70% TOC removal, the value taken as the limit for considering a solution biodegradable. As can be seen, after 28 days of bio-treatment, all the remaining solutions resulted biodegradable. The reason for testing reaction times longer than 555 min was the possibility of toxic or non-biodegradable reaction intermediates generation. That possibility can be dismissed from the experimental results. Thus, it can be concluded that partial mineralization of real MPG wastewaters with ozone produces intermediate solutions that are potentially treatable in a secondary biological step. Further investigation in a biological pilot-plant will be carried out to specify more details about such a possible coupling.
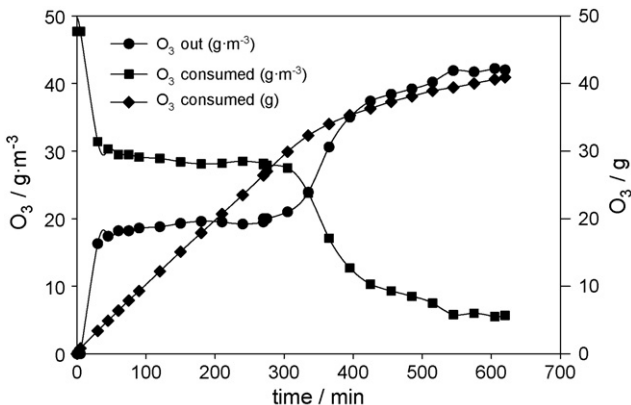

Fig. 8. Time-course of the ozone consumption (in terms of gas-phase concentration of ozone and total mass of ozone) and ozone leaving the reactor (in terms of gas-phase concentration) during the ozonation of MPG solution. Aqueous volume = 50.1 L, distilled H_2O, of O_3, O_2 flow = 200 L h^{-1}, [O_3]$_{gas-phase}$ = 47.7 g m^{-3}, unbuffered solution.
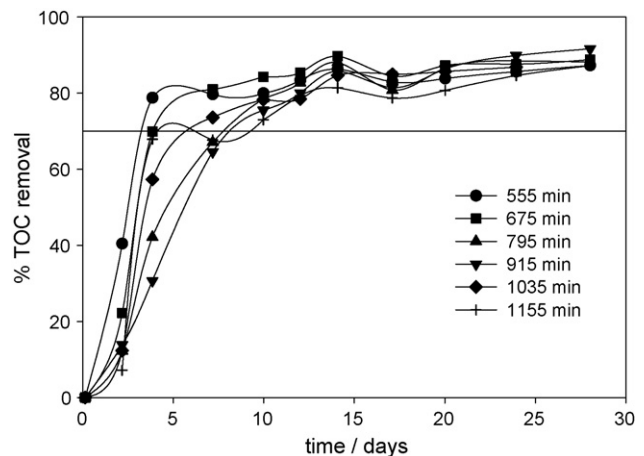

Fig. 9. Zahn–Wellens tests of solutions generated after 555, 675, 759, 915, 1035 and 1155 min of ozonation of MPG real wastewaters. Aqueous volume = 50.1 L, O_2 flow = 200 L h^{-1}, [O_3]$_{gas-phase}$ = 21.9 g m^{-3}, unbuffered solution.

4. Conclusions

The partial degradation of two different kind of pollutant solutions: (a) a mixture of five pesticides and (b) MPG, a compound used in chemical synthesis in the pharmaceutical industry, dissolved in distilled water, water with $35\,g\,L^{-1}$ of NaCl and real wastewater, have been carried out using a pilot-plant scale ozonation reactor. The study is framed in a large European project concerning the use of coupled chemical and biological treatments for the efficient removal of toxic or non-biodegradable pollutants in aqueous solutions. During the treatment of the pesticides mixture the ozonation is rather slow, complete removal of TOC is hard to achieve, chlorinated organics are not completely removed, and large amounts of ozone are spent in a process that is characterized by a poor mass transfer of ozone from the gas-phase to the solutions. In the case of the MPG treatment long ozonation times are required, but the kinetics is faster, and due to the fact that the final goal of the reaction is to generate intermediate solutions that could be amenable to a further biological treatment, the ozonation cannot be completely ruled out as a potential oxidation technology. In fact, tests of biodegradability applied to intermediate samples of the degradation of MPG show the suitability of the coupling. Further investigation will be needed for a more precise assessment of the possibilities of such a combined solution.

Acknowledgements

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