Ozonization of Acetochlor: Kinetics, By-Products and Toxicity of Treated Aqueous Solutions

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Ozonization of aqueous solutions of acetanilide type pesticide (acetochlor) was studied in a batch reactor operated at temperatures between 20 and 47 °C and ozone partial pressures from 236 to 488 Pa. Acetochlor mass concentrations were in a range between 1 and 200 mg L^{-1}. When the pH value of solutions was 5 or below, acetochlor decomposition was a result of its direct reaction with ozone, and the pesticide-decay data were well described by power-law kinetics: first-order with respect to acetochlor and 0.37 with respect to ozone concentration. The activation energy for the pesticide oxidation was found to be 67 kJ mol^{-1}. While acetochlor could be completely removed from the solutions, the total organic carbon (TOC) reduction was appreciably lower (35 %) due to the formation of ozone-resistant intermediates. The kinetics of TOC concentration reduction was found to obey a first-order process with two distinct steps, with an activation energy of 33 kJ mol^{-1} for the first step and 44 kJ mol^{-1} for the second step. Ozonization was also more effective under alkaline condition with addition of a co-oxidant such as Fenton reagent or hydrogen peroxide. The ability of ozone to oxidize the molecular structure of dissolved acetochlor resulted in an increase of biodegradability, demonstrated by an increase in the BOD$_5$/COD ratio, as well as in a reduced level of toxicity determined by the *Daphnia magna* test.

Key words:
Ozonization, pesticides, acetochlor, kinetics, toxicity, biodegradability

Introduction

The widespread use of pesticides in agricultural activities represents many potential sources for environmental pollution by these compounds. Among pesticides the triazine herbicides atrazine and simazine are the most common contaminants of both surface and ground waters. Since many pesticides are highly toxic and cannot be efficiently removed by conventional water treatment processes, advanced oxidation processes (AOPs) such as ozonization have recently received more attention as the most promising methods for pesticides degradation.

A report of Meijers *et al.* has shown that among 23 selected pesticides only 6 can be effectively decomposed by ozone at pH 7.2, using the ozone disinfection dosage (O$_3$/DOC) of 0.55 g/g.[1] Application of a higher ozone dosage (1.0 g/g) resulted in effective degradation for about 50 % of the tested pesticides. Pesticides were more effectively degraded at higher ozone dosages, higher pH values, and higher temperatures. Thus, atrazine, propazine, simazine, chlorfenvinphos, tetrachlorvinphos,

2,4-D, 2,4-DP, and 2,4,5-T were effectively decomposed at ozone dosage of 1.4 g/g and hydrogen peroxide dosages (H$_2$O$_2$/O$_3$) of 0.5 g/g. Furthermore, the study[1] has shown that pH has a minor effect on the degradation efficiency and that no further improvement is achieved if the hydrogen peroxide dosage is increased. Xiong and Graham studied oxidation of five herbicides and found that their reactivities to ozone decrease in the following order: MCPP, MCPA, 2,4-D, simazine, and atrazine at both acidic and neutral pH values.[2] Roche and Prados evaluated the oxidation efficiency of two systems, ozone and ozone combined with hydrogen peroxide, with 11 common pesticides. They found that ozone alone reacts rather poorly with the majority of tested pesticides.[3] However, ozone was found effective for aldicarb, terbutin and isoproturon, whereas the effectiveness for atrazine, malathion, HCB, aldrin, α-endosulfan, lindane, methyl-parathion, and linuron depends on conditions such as water characteristics and contact time. For example, tests with atrazine dissolved in groundwater showed that the contact time in combination with the ozone dosage is one of the most important parameters. On the other hand, the use of hydrogen peroxide enhanced the removal of all pesticides investigated. The weakening effect of oxidation in the presence

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of methanol as a scavenger was demonstrated in a study of atrazine ozonization.[4] The effect was attributed to the lower involvement of OH* radicals as compared to the direct O_3 reaction. The radical scavenger effect on atrazine ozonization in the presence of Mn(II) salt implied that the degradation of this pesticide follows a radical-type mechanism via hydroxyl radical species.[5] The rate coefficients for the direct reaction of ozone with 45 potential organic drinking water contaminants, including pesticides, can be found in a work of *Yao* and *Haag*.[6] The rate coefficients were measured in water in the presence of hydroxyl radical scavengers to minimize interfering radical chain reactions. Prado and Esplugas compared different AOPs involving ozone to eliminate atrazine and concluded that the best results are obtained at neutral and lower pH by employing either UV/H_2O_2 or $UV/H_2O_2/O_3$ systems.[7] At higher pH (10.1–11.7) ozonization was found the most effective process. It should be emphasized at this point that activation with UV radiation is suitable only for non-colored wastes.

Since atrazine is recognized as a refractory and toxic compound, it is expected to be substituted for by acetanilide pesticides, at least to some extend. The acetanilide pesticides are a group of chemically similar herbicides including alachlor, metolachlor, acetochlor, and others. There are already some reports on alachlor being employed in Italy after the ban of atrazine. This has encouraged a few research groups to study the transformation of alachlor and metolachlor.[8,9] In 1999 the EPA announced that the registration of acetochlor (2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide), a direct replacement for the established pre-plant grassy weed control chemicals, will result in a significant reduction in the total use of corn herbicides in the United States. Acetochlor has a broader spectrum of activity and can be applied at lower rates of application than the available alternatives. Acetochlor is likely to reduce the total amounts of herbicides applied to corn primarily by substituting for alachlor, metolachlor, atrazine, and 2,4-D. However, in spite of its potential to become a high priority pesticide, there are no data available on its use, possible metabolites, and appropriate techniques that are capable of reducing its concentration in water to permitted levels. According to the γ_{EC} directives for pesticides in drinking water, the permitted level is 0.1 μg L^{-1}. In order to overcome this lack of information, we have undertaken a laboratory study of acetochlor ozonization. The aim of the study was to determine the degradation kinetics as well as to check the biodegradability and toxicological properties of treated samples. Aqueous solutions of acetochlor were treated in the acidic region (pH 4.8–5.0), which is determined by the amount of dissolved chemical. Having these data available, it would be possible to judge whether ozonization is a feasible process for acetochlor degradation.

Experimental

Materials

Acetochlor (Zeneca, USA) was of 95.4 % purity. Other chemicals used were in the highest purity commercially available.

Apparatus and Procedure

Ozonization experiments were conducted in a 1.5 L mantled glass reactor, which operated in a semi-batch mode (Sovirel, FRA). Ozone was produced by an ozone generator WOK 5 (Sauter, Swiss) at maximum mass concentration of 10 g L^{-1} and was fed to the reactor through a porous disc placed at the reactors bottom. In all experiments the reactor was charged with 0.8 L of aqueous solution of pesticide, and this volume was kept constant throughout the experiments. The aqueous solution was prepared using deionized water conductivity κ = 1–3 μS cm^{-1}. The reactor was equipped with a turbine type impeller running at 1000 rpm.

Experiments were conducted at 20, 34, and 47 °C, ozone partial pressures of 236, 362, and 488 Pa, and pesticide mass concentrations between 1 and 200 mg L^{-1} (i.e. 0.623 to 124 ppm of organic carbon). To test whether ozonization of acetochlor was a mass transfer limited reaction, preliminary ozonization experiments were performed at 500, 1000 and 1500 rpm with different ozone flow rates. Since the ozonization rates were independent on these variables, it was concluded that the transport of ozone across the gas-liquid interface did not retard the measured oxidation rates.

In a typical run the ozone/air mixture was sparged through the aqueous solution of acetochlor charged into the reactor at a desired temperature. Dissolved ozone concentrations in the solution were determined by the indigo method[10] and by iodometry (DIN 19627). When the Fenton reagent or hydrogen peroxide was used as a co-oxidant, it was added into the solution before the ozone was introduced. In order to perform experiments at different but constant pH of the solution, the following buffers were used: a phosphate buffer to control pH at 7, a borate buffer to control pH at 10, and a citric acid buffer to control pH at 2. Aqueous samples (20 ml) from the reactor were withdrawn periodically and analyzed for residual content of acetochlor, total organic carbon (TOC), adsorbing organic halogens (AOX), and intermediates. Samples were also analyzed for biodegradability and toxicity.

Analysis

Acetochlor in solution was quantitatively determined by reversed-phase HPLC using a Hewlett--Packard 1100/DAD (set at 238 nm) system equipped with a Rheodyne 7725i injection valve (20 μL sample loop). The analyses were made using a 250 × 4.6 mm i.d. column filled with 0.5 μm C 18 (Kromasil) stationary phase. The mobile phase consisted of acetonitrile (550 ml), water (450 ml), 85 % H_3PO_4 (1 ml), and triethylamine (1 ml).

The organic carbon concentrations in aqueous samples were measured by an advanced HTCO Rosemount/Dohrmann DC-190 TOC analyzer, which was equipped with a non-dispersive infrared (NDIR) CO_2 detector.

AOX determination was performed according to the standard procedure of ISO 9562 using Dohrman's DX–2000 as an adsorbable organic halogens analyzer.

The identification of high molecular intermediate products was performed by means of a GC/MS analyzer Finnigan GCQ (Finnigan). Before analysis, Na_2SO_4 was added to a sample which was then extracted by dichloromethane. The resulted solution was injected into the GC. The GC was equipped with a HP Ultra-2 column and operated with initial column temperature of 38 °C for 1.5 min, then increased linearly to 300 °C at a rate of 15 °C min^{-1}, and held at the upper temperature for an additional 6 min. The injector temperature was 250°C. Electron ionization (electron impact by 70 eV) was used. The mass selective detector was adjusted to detect molecular mass in the range of 70 to 450. Helium carrier gas of ultrahigh purity was used with linear velocity of 45 cm s^{-1}.

Low molecular mass organic acids formed on ozonizator were identified and evaluated by means of ion chromatography using conductivity detector. An ion chromatograph model L-6200A (Merck-Hitachi) equipped with pre-column (Dionex, IonPac®AG4A-SC, 4 mm), column (Dionex, IonPac®AS4A-SC, 4mm) and suppressor (Dionex, ASRS ULTRA, 4mm) was used. Carbonate eluent at a flow rate of 2 mL min^{-1} and borate eluent at a flow rate 2 mL min^{-1} were used.

The chemical oxygen demand (COD) was determined by the closed reflux method; its concentration was measured colorimetrically and titrimetrically. The biochemical oxygen demand (BOD) was assessed by the standard dilution method using a commercially available special blend of bacterial cultures Bioseed (Interbio) as a seed source. Both COD and BOD tests were performed according to Standard Methods for the Examination of Water and Wastewater. The mean values of six measurements are quoted as results. The tests were repeated twice. As required by the standard method, all liquid samples were neutralized before BOD assessment.

The acute toxicity of ozonization products of acetochlor has been compared with the toxicity of pure acetochlor utilizing the *Daphnia magna* test according to the standard procedure ISO 6341.

Results and discussion

Ozonization

A typical time dependence of acetochlor concentration (expressed in terms of carbon content) as well as total organic carbon concentration in solution (TOC) is illustrated in Figure 1 for experiments carried out at three different temperatures. These experiments were performed with solutions at their natural pH, i.e. from 4.8 to 5.0. As can be seen, the acetochlor decay is quite rapid. Thus, in an experiment performed at 20 °C, 61 % of acetochlor was decomposed after 60 min of ozonization, whereas in this period of time complete conversion was attained at temperature of 47 °C. On the other hand, the TOC reduction achieved is low and does not depend strongly on temperature. For example, in the 20 °C experiment, only 11 % of initial carbon was converted into CO_2 and H_2O after 60 min, but about twice as much when the temperature was raised up 47 °C.
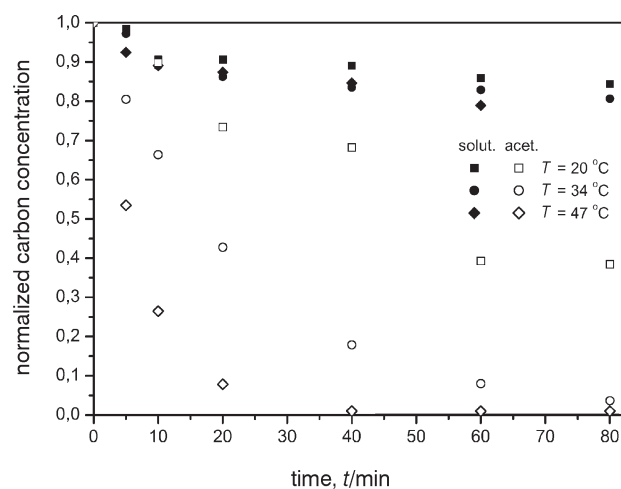

F i g . 1 – *Organic carbon concentration in acetochlor and in solution (TOC) as a function of time in ozonation experiments carried out at different temperatures: p_{O_3} = 488 Pa; $\gamma_{acet,0}$ = 100 mg L^{-1}*

The difference between the carbon due to acetochlor and that in the solution accounts for the intermediate products formed during the course of ozonization. A typical accumulation of intermediate products for the two experiments performed at different initial concentrations of acetochlor is depicted in Figure 2, together with TOC in solution and carbon due to acetochlor. It can be concluded from this figure that acetochlor was mainly converted into the intermediate products, which were
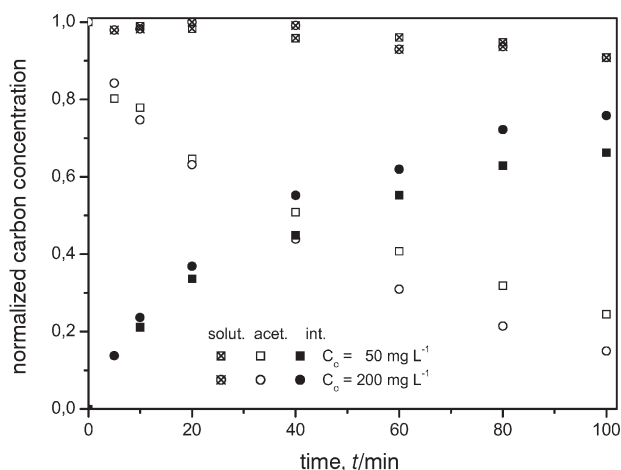
F i g . 2 – *Organic carbon concentration in acetochlor, in solution (TOC), and accumulated carbon in intermediates as a function of time in ozonization experiments carried out at two different initial acetochlor concentrations: T = 20 °C; p_{O_3} = 488 Pa*

poorly converted to carbon dioxide under the conditions employed.

Speculated Reaction Scheme

The tentative products identified by means of GC/MS analysis were unstable dealkylated acetochlor and dialkylchloride of carbamic acid that degrade into the following intermediates identified by ion chromatography: acetic, chloroacetic, and formic acids as well as chloride and nitrate ions. The portion of carbon derived from the three acids was found to be 13.4 % of the total organic carbon (TOC) after 30 min of treatment and increased to

17.3 % after 60 min. Since the pH of unbuffered solutions during the ozonization process was always kept in the acidic region, (it dropped from 5 to 3), ozone was not decomposed into hydroxyl radicals. Therefore one can speculate that ozone had reacted in a molecular form or by a so-called direct reaction. However, the identified intermediates allow us to speculate with a simple reaction scheme such as shown in Figure 3.

Ozonization of acetochlor appears to involve electrophilic ozone attack at the ether as well as carbonyl groups.[11] Reaction at the ether group can be explained by ozone attack on the carbon-hydrogen bonds. It is, however, generally agreed that ozonization yields a hydrotrioxide intermediate, but the exact mode of formation of this intermediate and how it converts further to products is still unclear.[12] However, in the case of acetochlor ozonization it probably decomposes after a loss of oxygen yielding the appropriate aldehyde and alcohol, which are further oxidized to acetic acid which was identified in this work. A similar mechanism was proposed for ozonization of methyl tertiary-butyl ether and ethyl tertiary-butyl ether.[13] Due to chloride ions and chloroacetic acid being found as intermediate products, it appears that the reaction of electrophilic molecular ozone with the carbonyl group also occurs.

Kinetics

As discussed above, ozone reacts with acetochlor directly at a pH lower than 5. Therefore one can write an equation for the acetochlor disappearance rate in the following power-law form
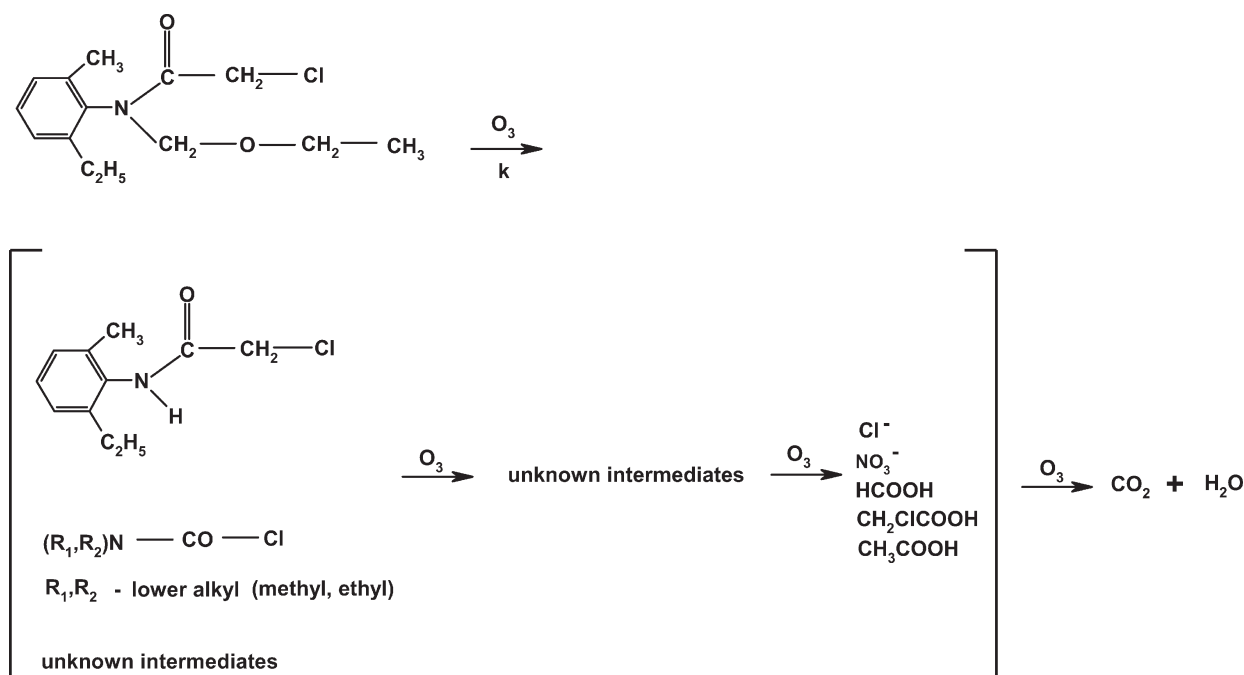

F i g . 3 – *Simplified reaction pathway of acetochlor oxidation by ozone in aqueous solution*

$$-\frac{\mathrm{d}\gamma_{\text{acet.}}}{\mathrm{d}t} = k\,\gamma_{\text{acet.}}^{m}\,\gamma_{O_3}^{n} \qquad (1)$$

in which $\gamma_{\text{acet.}}$ and γ_{O_3} represent the acetochlor and ozone mass concentration (mg L^{-1}) in aqueous solution. A similar expression can be written also in terms of the concentration of total organic carbon (TOC) in solution (mg L^{-1}). Since the experiments were carried out at constant partial pressure of ozone, equation (1) can be further simplified to

$$-\frac{\mathrm{d}\gamma_{\text{acet.}}}{\mathrm{d}t} = k^{*}\,\gamma_{\text{acet.}}^{m}. \qquad (2)$$

when the apparent rate coefficient k^{*} (min^{-1}) stands for the product of the rate constant and the ozone concentration to the order n. Many experimental investigations have found that the oxidation rate in the acidic region is a first-order reaction with respect to the organic substrate.[6,14] Thus, if one assumes the acetochlor disappearance rate to be a first-order reaction with respect to its concentration ($m = 1$), then the experimental data plotted according to the integrated form of Eq. (2) must yield a straight line. A first-order kinetic plot is shown in Figure 4 for the acetochlor decay at three different temperatures. For the TOC parameter, two distinct first-order rate processes are demonstrated in Figure 5. Since the experiments were performed at three different ozone partial pressures, one can also estimate the order of the reaction with respect to ozone by plotting ln (k^{*}) vs. ln (γ_{O_3}). The resultant order with respect to ozone ($n = 0.37$) is illustrated in Figure 6, where k^{*} plotted against $\gamma_{O_3}^{0.37}$ is a straight line. Within the experimental error this value can be considered 0.33 and suggests that the very first step of acetochlor decomposition is a direct molecular reaction between acetochlor and oxygen resulting from ozone decomposition. Contrary, when all or-
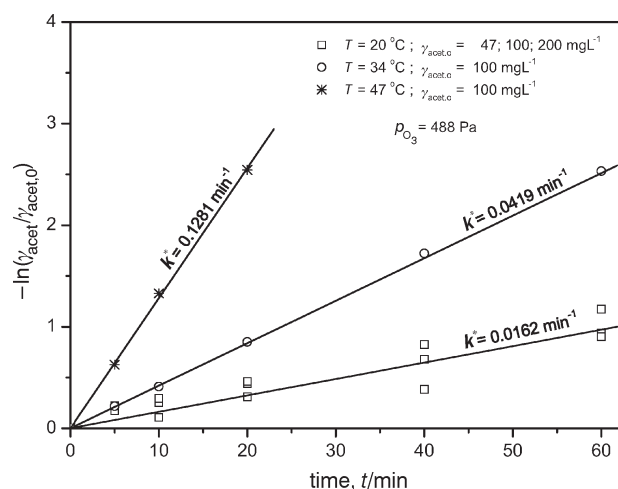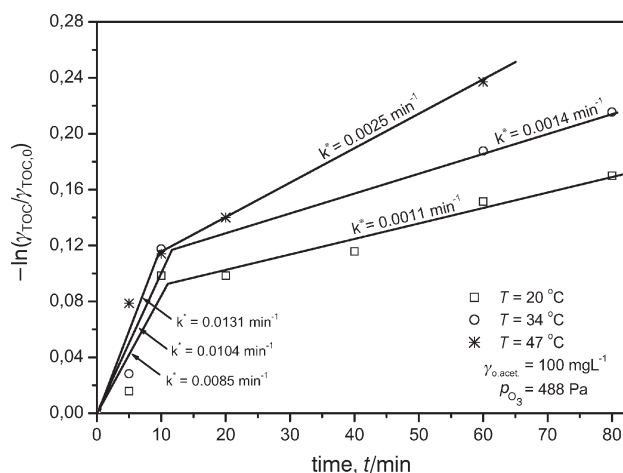

Fig. 5 – *First-order kinetic plot for acetochlor oxidation by ozone based on total organic carbon (TOC) concentration measurements*
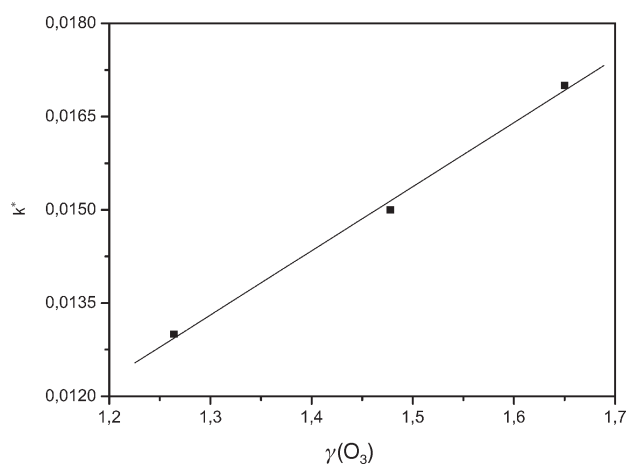

Fig. 6 – *Apparent oxidation rate constant as a function of ozone partial pressure*

Fig. 4 – *First-order kinetic plot for acetochlor oxidation by ozone based on pesticide concentration measurements*

ganic species present in solution are simultaneously oxidized with ozone, the order with respect to ozone should be higher, because the products resulting from acetochlor decomposition consume additional ozone. In literature it was mostly found to be a first-order dependence.[6,14] The Arhenius plots (Figure 7) for the acetochlor decay yielded the activation energy of 67 kJ mol^{-1}. For the TOC reduction, the activation energies were found to be 33 kJ mol^{-1} for the first step and 44 kJ mol^{-1} for the second step. The higher value of the activation energy exhibited with the second-step for the TOC reduction suggests that the intermediate products formed in the reaction between acetochlor and ozone are more stable, which consequently resulted in low TOC reduction in comparison to the decomposition of acetochlor (see Figure 2). However, from the data on Figure 5, it is obvious that the activation energy for the first step cannot be evaluated with a high degree of certainty due to the low number of data points. Furthermore, in the estimation of acti-
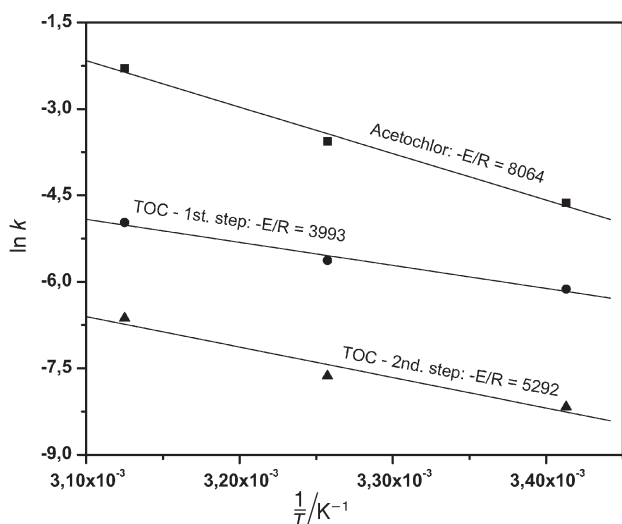
F i g . 7 – *Arrhenius plot for ozonization of acetochlor and all organic compounds (TOC) present in solution*

F i g . 8 – *Organic carbon concentration in acetochlor and in solution as a function of time in ozonization experiments carried out at different solution pH values: T = 20 °C; p_{O_3} = 488 Pa; $\gamma_{acet\ 0}$ = 150 mg L^{-1}*

vation energy for the TOC reduction, a first-order dependence with respect to ozone was assumed in both steps. Unfortunately, in the open literature there is no data for the activation energy for ozonation of acetochlor, or for a similar compound. The only comparison can be made with atrazine, for which the second-order rate coefficient for the direct reaction with ozone (2 < pH < 6) was reported to be 6 L mol^{-1} s^{-1}.[6] Assuming the first-order dependence with respect to the ozone concentration in the present work (instead of 0.37), one can calculate a rate coefficient of approximately $k = 5$ L mol^{-1} s^{-1} at about the same temperature, which is the same order of magnitude. The rate coefficients for the reactions between organics and their degradation products with OH radicals can be even 9 orders of magnitude higher.[15]

Influence of pH

Since pH is the key quantity for the stability of O$_3$ in aqueous solution it is important to examine also its influence on the rate of acetochlor decomposition. The ozonation results obtained with solutions having different pH values are illustrated in Figure 8. As can be seen, acetochlor as well as TOC in solution reacted at quite different rates under acidic or basic conditions. At a pH of 10 and temperature of 20 °C, the acetochlor concentration reached zero value after only 10 minutes of ozonation. Thus, it is evident that hydroxyl radicals formed due to the faster ozone decomposition in the basic region appreciably accelerated the rate of acetochlor decomposition. It can be seen that the TOC reduction is also higher under basic conditions. In agreement with previously mentioned investigations the results in Figure 8 clearly demonstrate that the efficiency of acetochlor removal is
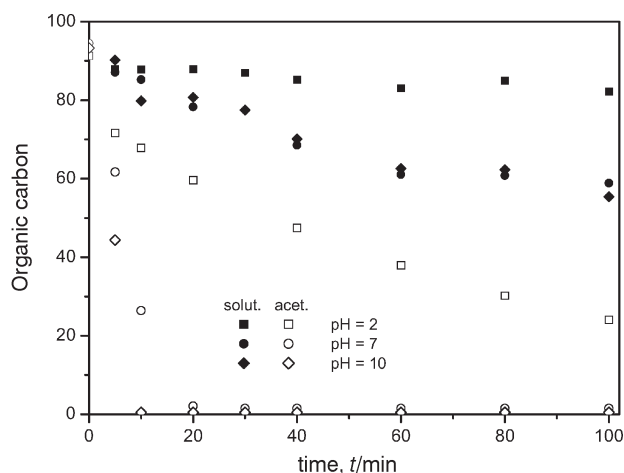
higher when ozonation is carried out under basic conditions. However, lower TOC reduction indicates the presence of significant amounts of degradation products, even under basic conditions.

Environmental regulations also limit the amounts of highly toxic organochlorinated compounds (AOX) present in drinking as well as in wastewaters. It is therefore important that an oxidation process is capable of decreasing the AOX concentration. In order to find the most effective advanced oxidation process from AOX concentration point of view, the decrease of AOX concentration was studied for pure ozonization, ozonization with Fenton reagent, and ozonization with hydrogen peroxide. Comparison of these results with the results obtained with ozone alone is given in Figure 9. As shown, an appreciable decrease of AOX concentration attained at pH 10 can be further improved by adding a small quantity of hydrogen peroxide.
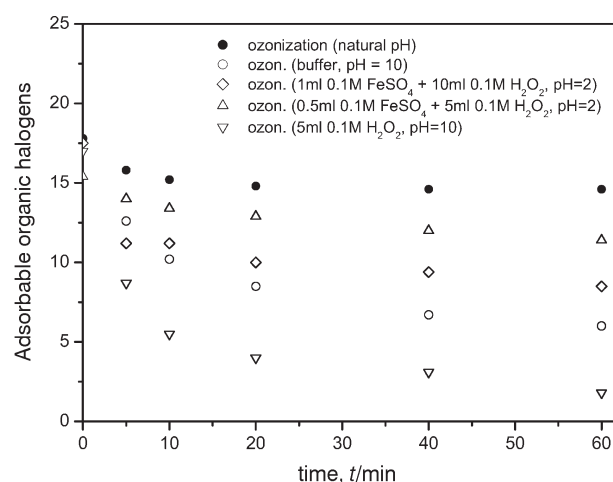

F i g . 9 – *Adsorbable organic halogens as a function of time in ozonization experiments carried out with different co-oxidants: T = 20 °C; p_{O_3} = 488 Pa; $\gamma_{acet,\ 0}$ = 150 mg L^{-1}*

Biodegradability and toxicity

The biodegradability of liquid samples taken during ozonization at different times was assessed by the BOD_5/COD ratio, where BOD_5 means biochemical oxygen demand after 5 days and COD means chemical oxygen demand. Figure 10 illustrates the dependence of both types of oxygen demands (COD and BOD_5) as well as BOD_5/COD ratio on the time of ozone treatment for two initial concentrations of acetochlor. As can be seen, BOD increased while COD decreased slightly with the treatment time. Thus, the increase of BOD_5/COD ratio is obviously caused by both BOD_5 increase and COD decrease. Generally low BOD_5/COD ratios attained during ozonization may be attributed to the low metabolic values of formed acids. Nevertheless, these results demonstrate that slightly more compounds amenable to the biological treatment were formed during the treatment by ozone, as evidenced by the increase in BOD_5.
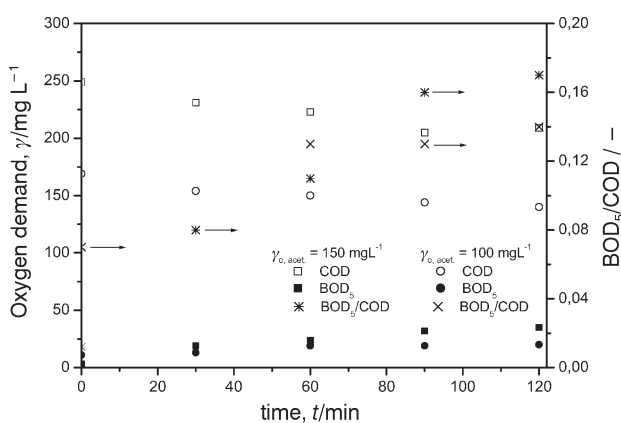

F i g . 1 0 – *Oxygen demands (COD and BOD_5) and BOD_5/COD values as a function of ozone treatment time for two initial acetochlor concentrations: $T = 20\ °C$; $p_{O_3} = 488\ Pa$*

The acute toxicity of products formed during ozonization was studied using *Daphnia magna*. The results (Table 1) indicate that the concentration of solution ozonizated at natural pH, which immobilizes 50 % of the exposed *Daphnia magna* in 24 h, is higher after 60 minutes of ozonization. Therefore, it is obvious that products of ozonization are less toxic to *Daphnia magna* when compared to the toxic properties of the mother compound. Thus, the detoxification achieved by ozone treatment has increased potential of ozonization as an efficient process for removal of acetochlor and similar compounds in water.

T a b l e 1 – *Results of toxicity tests by Daphnia magna.*

Ozonization time, min	0	30	60
$\gamma_{EC50(24h)}$, mg L^{-1}	6.3	16.0	20

Conclusions

Acetochlor could be efficiently degraded by ozone added to an aqueous solution. During the ozonation of acetochlor, several ozone resistant intermediates are formed. Among these intermediates low molecular weight acids are the oxidation products, which cannot be readily oxidized to carbon dioxide. Rapid acetochlor decay under acidic conditions can be described by first order kinetics, while disappearance of intermediates by means of TOC was found to follow two distinct first-order rate processes. pH has an important influence on the rate of acetochlor decomposition as well as on the disappearance rate of TOC. The process of acetochlor decomposition could be accelerated by adding hydrogen peroxide.

A slight increase in the biodegradability of acetochlor solutions is observed upon treatment with ozone. Lower AOX and EC50 (24 h) values clearly demonstrate that ozonization is an efficient technology for detoxification of waters that contain the acetanilide pesticide acetochlor.

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