

Calibration of full-scale ozonation systems with conservative and reactive tracers

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ABSTRACT: A full-scale ozonation reactor was characterised with respect to the overall oxidation budget by coupling laboratory kinetics with reactor hydraulics. The ozone decomposition kinetics and the ratio of the OH radical to the ozone concentration were determined in laboratory batch experiments. With the computer model AQUASIM these parameters could be coupled with the hydraulics of the ozonation reactor which allowed the prediction of the behaviour of ozone, chlorine, and micropollutants (e.g. atrazine) in the reactor. The comparison of measured and modelled concentration showed an excellent agreement. The present study summarises a general approach of how full scale ozonation reactors can be calibrated to assess disinfection, oxidation and minimise disinfection by-products, such as bromate

INTRODUCTION

The disinfection of drinking waters has recently been challenged by micro-organisms (e.g. *Cryptosporidium*) which are difficult to inactivate by conventional disinfectants. From all the disinfectants applied in drinking water treatment ozone is most efficient with respect to inactivation of *Cryptosporidium*. However, relatively high exposures of ozone are required to get, e.g. a 2-log inactivation. The inactivation of *Cryptosporidium* would not be that big of a problem if there was not the simultaneous formation of bromate in bromide-containing waters. With the discovery of the potential carcinogenicity of bromate therefore a new phase has been entered in ozone-based drinking water treatment. Instead of just optimising disinfection and oxidation according to the philosophy 'the more the better', minimal formation of disinfection by-products (mainly bromate) has to be guaranteed. The mechanism for bromate formation is rather complicated and includes both molecular ozone and OH radical reactions, where OH radicals stem from the naturally occurring ozone decomposition in aqueous solutions [1,2].

To optimise an ozonation process it is therefore necessary to guarantee disinfection (mainly molecular ozone reactions) and oxidation (molecular ozone and OH radicals) while minimising bromate formation (molecular ozone and OH radicals). However, this is only possible if we know the concentration of the two main oxidants, ozone and OH radicals. The ozone concentration in an ozonation reactor can be directly determined by electrochemical or colourimetric methods. Natural organic matter and carbonate/bicarbonate are the major sinks for OH radicals in drinking waters and generally lead to concentrations in the order of $< 10^{-12}$ – 10^{-13} M for standard ozonation processes. These very low concentrations are not directly accessible by standard analytical techniques (e.g. UV-VIS spectrometry, HPLC, etc.). To overcome this problem we have developed a new concept (R_{ct} -value) which makes it

possible to determine the ratio of the concentration of ozone and OH radicals for an entire ozonation process. With this we can describe the oxidation processes in bench-scale experiments [3]. To describe a full-scale system with regard to its ozone and OH radical oxidation capacity, we have to link reaction kinetics with the hydraulic characteristics of a particular reactor by a computer simulation. For this purpose we have applied the program AQUASIM which was developed at EAWAG [4].

To test our concept, we have selected a water treatment plant in the city of Zürich (Switzerland) where we coupled the hydraulic properties (determined by a conservative tracer) with the oxidation chemistry which was calibrated with reactive tracers. We used the decomposition of ozone, the formation of chlorate from chlorine and the degradation of a micropollutant (atrazine) as reactive tracer reactions.

In short, our approach includes the following steps:

- Laboratory ozonation experiments to determine the first-order rate constant for ozone decomposition and the R_{ct} -value (ratio of OH radical and ozone concentration during the ozonation experiment).
- Determination of rate constants for the reaction of micropollutants with ozone and OH radicals at the appropriate treatment temperature.
- Characterisation of the hydraulics of the ozonation chamber with a conservative tracer and fitting of the breakthrough curves with a series of ideal reactors (plug flow and completely stirred tank reactor (CSTR)) with AQUASIM as a tool.
- Coupling of the reactor hydraulics with chemical kinetics.

With these four steps the characterisation of ozonation reactors could be carried out. The evolution of ozone, micropollutants and chlorate in the reactor could then be calculated with the AQUASIM code. The calculated concentration profiles were compared with measurements at different locations within the reactor by sampling for probe compounds (atrazine and chlorate).

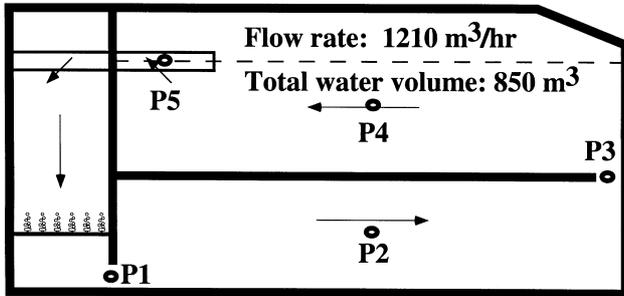


Fig. 1 Schematic representation of ozonation reactor of the lake water treatment plant of the city of Zürich (Lengg). P1–P5 are sampling points within the reactor.

MATERIALS AND METHODS

The analysis of standard water quality parameters (pH, alkalinity, DOC, etc.) was performed by standard methods. For full-scale experiments the following additional parameters had to be measured: ozone, OH radicals, atrazine and chlorate.

The ozone concentration was determined by the indigo method [5]. The OH radical concentrations in laboratory experiments was determined via the addition of an *in situ* probe compound (p-chloro benzoic acid, pCBA) which allowed to determine the R_{ct} -value in the laboratory. This allows the calculation of the OH radical concentration if the ozone concentration is known [3,6]. The concentration of pCBA was monitored by reverse-phase HPLC (using a 55:45 methanol:10 mM H_3PO_4 buffer eluent, at 1 mL/min, and UV-detection at 234 nm). With a 300- μ L injection, the detection limit was 0.025 μ M. Atrazine was measured by GC-MS after pre-concentration with solid phase extraction, with a detection limit of approximately 1 ng/L. Chlorate was measured by IC (carbonate eluent, AS9-SC column) with conductivity detection (detection limit 10 μ g/L).

Ozone reactor and water characteristics

The full scale experiments were performed in an ozonation reactor as shown in Fig. 1 (city of Zürich, Switzerland). The ozonation step consists of a first reaction chamber where the ozone gas-liquid transfer occurs, followed by two contact chambers where reactions with the dissolved ozone can occur. Within the reactor there were 5 sampling points (P1–P5) where samples could be taken for the analysis of ozone and probe compounds. The ozonation step under investigation is the first ozonation (pre-ozonation) in the whole treatment train. There was no treatment prior to this step and it was followed by rapid sand filtration, intermediate ozonation, BAC filtration, slow sand filtration and adjustment of pH with lime water. The main

Table 1 Characteristics of the ozone reactor

O ₃ transfer chamber (m ³)	Contact chambers		Total HRT (min)	Water type
	(Number)	(m ³)		
165	2	420 and 438	25–50	lake water

characteristics of the ozonation step under consideration in the present study are shown in Table 1. The hydraulics of the ozone reactor was characterised by tracer tests with sodium chloride. The breakthrough curves were fitted with the AQUASIM code.

The water treated is a lake water (lake Zürich) with low DOC (approx. 1.3 mg/L) and relatively low alkalinity (2.6 mM HCO_3^-) with an average pH of 7.8 and a temperature of 5–7 °C. This water contains only minor concentrations of micropollutants, all of them are far below the drinking water standards. The only micropollutant which could be used in this study was atrazine with concentration below 10 ng/L. The water composition of the lake water remains constant throughout the year.

RESULTS AND DISCUSSION

Characterisation of ozonation processes with respect to ozone and OH radical (\bullet OH) concentrations in laboratory-scale experiments

The experimental approach of using an OH radical probe (\bullet OH-probe) compound to measure the steady-state \bullet OH concentration in aqueous systems is well established. In the context of an ozonation system, the ideal \bullet OH-probe reacts only with \bullet OH, and not significantly with O₃ or other reaction species. Thus, the disappearance of the probe is an indirect measure of the OH concentration. For these experiments, p-chlorobenzoic acid (pCBA) was used for the \bullet OH-probe; it has a very low reactivity with O₃ ($k_{O_3/pCBA} = 0.15$ M/s), but reacts readily with OH ($k_{OH/pCBA} = 5 \times 10^9$ M/s [3]).

If the probe compound M is at very low concentrations ($k_M[M] \ll \sum k_{S_i}[S_i]$) then the presence of M does not significantly contribute to the overall scavenging of OH, and

$$\text{total rate of } \bullet\text{OH scavenging} \approx \sum k_{S_i}[S_i][\bullet\text{OH}] \quad (1)$$

$\sum k_{S_i}[S_i]$ represents the overall concentration of \bullet OH scavengers (promoters and inhibitors), M represents a probe compound (or micropollutant) present at low concentrations, and k_{S_i} and k_M represent the individual rate constants for the OH reaction with S_i and M, respectively.

Because the probe compound pCBA has a very low reactivity with O₃ but reacts rapidly with OH,

$$\frac{-d[\text{pCBA}]}{dt} = k_{\bullet\text{OH}/\text{pCBA}}[\text{pCBA}][\bullet\text{OH}] \quad (2)$$

Rearranging and integrating Eqn 2 obtains

$$\ln\left(\frac{[\text{pCBA}]_t}{[\text{pCBA}]_0}\right) = -k_{\bullet\text{OH}/\text{pCBA}} \int_0^t [\bullet\text{OH}] dt \quad (3)$$

where the term $[\bullet\text{OH}]dt$ represents the time integrated concentration of $\bullet\text{OH}$, or the $\bullet\text{OH}\text{-ct}$. Therefore, the relative decrease in concentration of a probe compound at any time t is an indirect measurement of the $\bullet\text{OH}\text{-ct}$, or 'hydroxyl radical exposure' at that reaction time. We can define a term, R_{ct} , which describes the ratio of $\bullet\text{OH}\text{-ct}$ and $\text{O}_3\text{-ct}$

$$R_{\text{ct}} = \frac{\int [\bullet\text{OH}] dt}{\int [\text{O}_3] dt} \quad (4)$$

where $[\text{O}_3]dt$ is the $\text{O}_3\text{-ct}$ or 'ozone exposure.' The ozone exposure can be calculated from the integral of ozone concentration vs. time data [1]. Substitution of Eqn 4 into Eqn 3 gives

$$\ln\left(\frac{[\text{pCBA}]_t}{[\text{pCBA}]_0}\right) = -k_{\bullet\text{OH}/\text{pCBA}} R_{\text{ct}} \int_0^t [\text{O}_3] dt \quad (5)$$

which shows that the ratio of the $\bullet\text{OH}\text{-ct}$ and the $\text{O}_3\text{-ct}$ (i.e. R_{ct}) can be calculated from the experimentally measured decrease in concentration of pCBA and O_3 . By plotting the left-hand side of Eqn 5 vs. the $\text{O}_3\text{-ct}$, the ratio R_{ct} can be backed out from the slope of the plot. In addition, because of the kinetic approach of this method, the $\bullet\text{OH}\text{-ct}$, $\text{O}_3\text{-ct}$, and R_{ct} values can be calculated as a function of ozonation time.

The stability of ozone in natural waters strongly depends on the water matrix. Water quality parameters such as pH, temperature, DOC, alkalinity may significantly influence the half-life $t_{1/2}$ of ozone in a particular water. In our empirical method all these effects are included without the need for introducing fitting parameters. Such parameters have to be introduced frequently if ozonation processes are characterised based on kinetic modelling only. Ozone decay experiments were performed at 5 °C which is the average temperature of the treated lake water in a depth of 30 m. Figure 2a shows an ozonation bench scale batch experiment of lake Zürich water at 5 °C.

The decrease of ozone at pH 8 after a dosage of 1 mg/L ozone is shown together with the decrease of pCBA which was added as a probe compound. Figure 2b shows the first-order representation of the ozone decrease. The first-order rate constant for the decrease of ozone was $k = 10^{-3}/\text{s}$ which corresponds to a half-life of ozone in the order of 10 min. In Fig. 2b it can be seen that the decrease of ozone is not first-order during the initial phase of the ozonation. Only after a first spontaneous ozone demand (30 s to 2 min) a first-order representation leads to a linear plot.

As discussed above, the decrease of pCBA, which only reacts with OH radicals and not ozone, is a measure for the integral exposure to OH radicals. Figure 3 shows a plot of Eqn 5 for the same experiments as shown in Fig. 2 which results in a

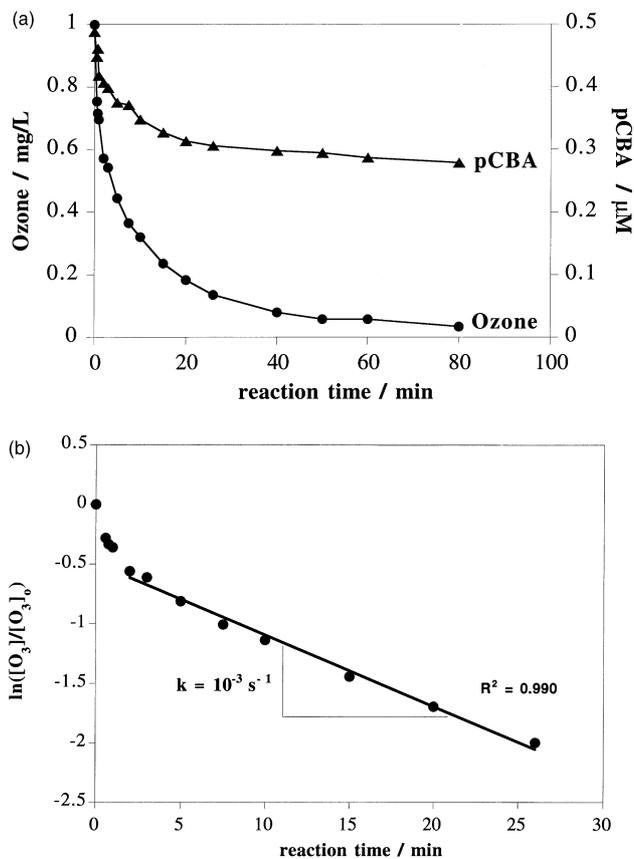


Fig. 2 (a) Decrease of Ozone and pCBA (p-chloro benzoic acid) in lake Zürich water (5 °C, pH 8, ozone dose 1 mg/L). (b) First-order decrease of ozone ($k = 10^{-3}/\text{s}$).

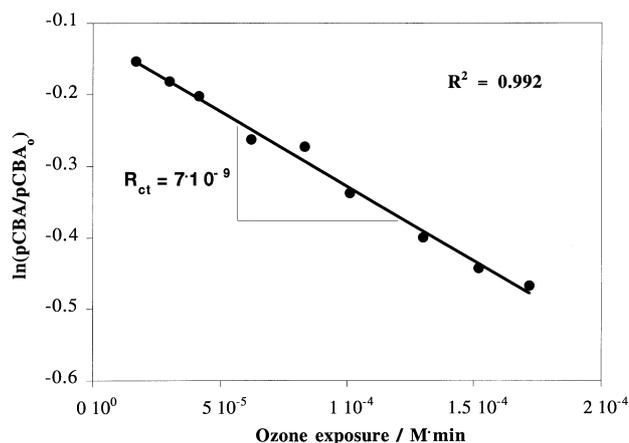


Fig. 3 Ozonation of lake Zürich water (5 °C, pH 8, ozone dose 1 mg/L). Representation of Eqn 5 resulting in the ratio R_{ct} of the concentrations of OH radicals and ozone.

$R_{\text{ct}} = 7 \times 10^{-9}$. This allows us now for the secondary phase to assess an ozonation process with respect to oxidation by ozone and OH radicals. If the R_{ct} is constant it represents directly the ratio of the concentrations of OH radicals and ozone. With this

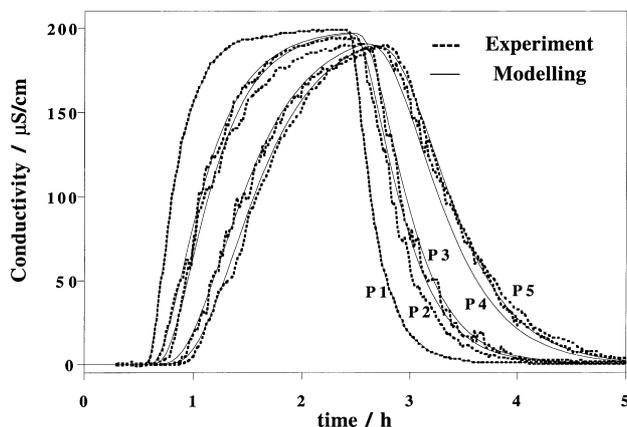


Fig. 4 Breakthrough curves for a conservative tracer (NaCl) in the ozonation: experimental data (dotted lines) and model calculations (solid curves) for five equidistant sampling points P1–P5.

we can estimate the transient steady-state concentration of OH radicals from the measurement of the ozone concentration. For an ozone concentration of 0.5 mg/L (10^{-5} M) the corresponding OH radical concentration is 7×10^{-14} M. This shows that OH radical concentrations are extremely low which has to be considered if the rate of oxidation of micropollutants by these oxidants has to be estimated. Also with respect to disinfection their effect can be neglected since their concentrations are so small.

Coupling of laboratory experimental data with full-scale experiments

The information on the ozone degradation kinetics and the ozone and OH radical oxidation capacity can now be used to predict oxidation processes in full-scale systems. The kinetic information has to be coupled with the hydraulics of the ozonation reactor.

Description of the hydraulics of the ozonation reactor

The ozonation reactor was hydraulically characterised by a continuous addition of sodium chloride and the measurement of the breakthrough curves at five sampling points (P1–P5) within the reactor (Fig. 1). All sampling points P1–P5 are located equidistant to each other. The breakthrough of the tracer was monitored by conductivity which is shown by the dotted lines in Fig. 4. Breakthrough of sodium chloride shows an asymmetric behaviour. Even though the sampling point P2 is in the middle between P1 and P3, the breakthrough occurs almost at the same time at P2 and P3. The same behaviour is observed for sampling points P4 and P5. Therefore, the hydraulics of the reactor has to be approached by a combination of a series of mixed reactors with a high degree of back-mixing. The ozonation reactor could be best modelled by an advection diffusion reactor for the ozone transfer chamber,

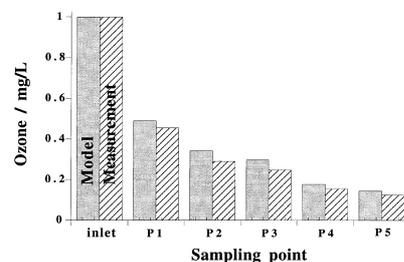


Fig. 5 Measured and modelled ozone profiles in lake Zürich water ozonation reactor.

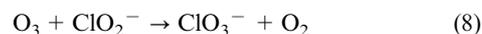
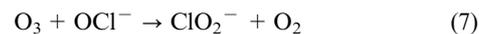
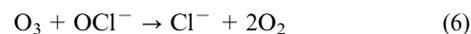
followed by the two contact chambers. The first of them was modelled as a series of four CSTRs (completely stirred tank reactors) whereas the second was approached by an advection diffusion reactor. In both contact chambers a high back flow had to be included to account for back mixing. The model calculations performed with the program AQUASIM are also depicted in Fig. 4 (solid lines) and show a good fit of the measured data.

Decomposition of ozone: ozone as a reactive tracer

The first-order rate constant for the decomposition of ozone ($k = 10^{-3}$ /s) which was determined above in a laboratory batch system, can now be used to model the ozone profile in the ozonation reactor if the decomposition kinetics are coupled with the hydraulics of the reactor. A comparison between ozone measurements and model calculations in the lake Zürich water ozonation reactor are shown in Fig. 5. The model predictions and the measurements are in almost perfect agreement which shows the potential of our approach. From a combination of bench-scale ozonation experiments with full-scale modelling it is therefore possible to characterise an ozonation reactor with respect to the overall ozone budget. This can also be applied to dynamically model disinfection processes if the corresponding kinetics are known. The ozone concentration in the gas-liquid contactor was calculated by assuming a linear increase of the ozone concentration from the top to the bottom of the reactor. This behaviour could be confirmed by pilot-scale measurements in gas-liquid contactors [7].

Ozone–chlorine reaction: chlorine as a reactive tracer

The reaction of aqueous chlorine with molecular ozone is well known and can be described by the following mechanism [8]:



The rate constants for reactions (6)–(8) are well established with $k_1 = 110/\text{M}\cdot\text{s}$, $k_2 = 30/\text{M}\cdot\text{s}$ and $k_3 > 10^5/\text{M}\cdot\text{s}$ at 25 °C.

Table 2 Half-life $t_{1/2}$ of aqueous chlorine during ozonation

Ozone concentration (mg/L)*	$t_{1/2}$ (chlorine) (s)	
	pH 7	pH 8
0.2	5900	1656
0.5	2365	662
1.0	1182	331

* Ozone concentration is considered constant during ozonation process.

According to the above mechanism, approximately 78% of the ozone reacts with hypochlorite (OCl^-) to chloride (Cl^-) and 22% to chlorite (ClO_2^-). Chlorite is then rapidly further oxidised to chlorate (ClO_3^-) by ozone. The equilibrium reaction (9) is important for the overall kinetics of the reaction since ozone only reacts with the deprotonated form OCl^- . To illustrate the importance of pH and ozone concentration on the half-life of aqueous chlorine in an ozonated water, some calculations for relevant water treatment conditions are shown in Table 2. At a pH of 7 and a small concentration of 0.2 mg/L of ozone the half-life of aqueous chlorine is almost two hours whereas for a higher ozone concentration of 1 mg/L and a pH of 8 it is only approximately 5 min.

The reaction kinetics given above were measured at 25 °C and have to be reconsidered for lower temperatures since the treated lake water has only a temperature of 5 °C. With an activation energy of 60 kJ/mol the first-order rate constants can be calculated as $k_1 = 20/\text{M/s}$ and $k_2 = 5/\text{M/s}$. In addition to these molecular ozone reactions, there are also OH radical reactions which may play an important role for chlorate formation. However, under our treatment conditions they can be neglected (see below).

In the intake pipe for lake water in the treatment plant of Zürich Lengg, the addition of a high dosage of chlorine (10 mg/L) is carried out once a month to avoid the growth of migratory shells which can lead to a complete clogging of the intake pipe [9]. After a few hours, during which chlorine can act in the intake pipe a residual of approximately 5 mg/L remains. When the pumps of the water treatment plant are turned on again, a plug of chlorine gets into the ozonation reactor. Therefore, our reactive chlorine tracer experiments could be carried out during a routine operation of the water works without any further additions of chemicals to the drinking water. The high concentration of chlorine applied to the water also guaranteed that only reactions with molecular ozone and no OH radical reactions are involved. Figure 6 shows breakthrough curves of chlorate during one of the high dosage experiments in the water works of Zürich (symbols). The chlorate concentration increases from P1 to P3 due to reactions (6)–(9) until all the ozone is consumed. Thereafter, no further increase of the

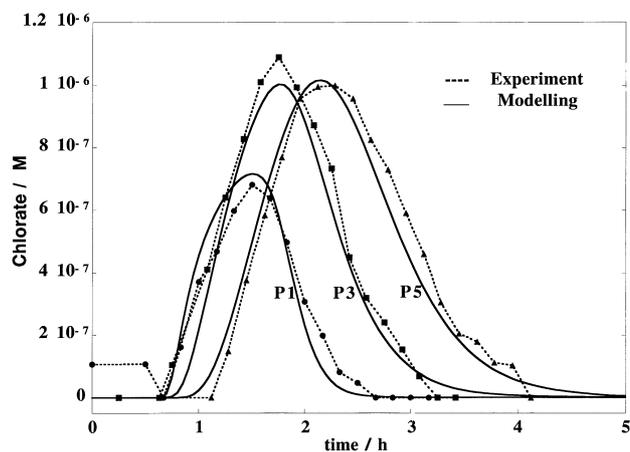


Fig. 6 Chlorate formation during a prechlorination experiment: Experimental data (dotted lines) and model calculations (solid lines).

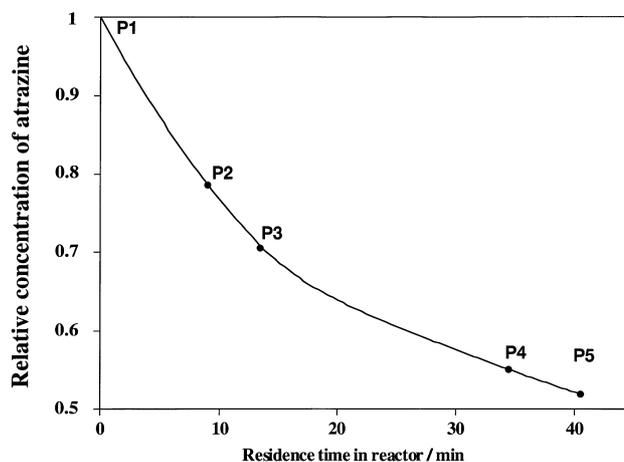


Fig. 7 Calculated degradation of atrazine in the ozonation reactor of lake Zürich (5 °C, pH 8, ozone dosage 1 mg/L).

chlorate could be determined. The comparison of experimental results (symbols) with the model calculations (lines) shows an almost perfect overlap. This shows that it is possible to directly transfer molecular kinetics to a full-scale system if they are coupled with reactor hydraulics.

Oxidation of organic micropollutants: OH radical probes

Depending on the rate constants of the oxidation of micropollutants with molecular ozone and OH radicals, their oxidation can occur either predominantly by ozone, OH radicals or a combination of both oxidants. Figure 7 shows the calculated relative decrease of atrazine in the ozonation reactor at 5 °C. The rate constants for the molecular ozone and OH radical reaction were 4 and $3 \times 10^9/\text{M/s}$, respectively [10]. The relatively low rate constant for the oxidation of atrazine by molecular ozone leads to a predominant oxidation via the OH radical pathway.

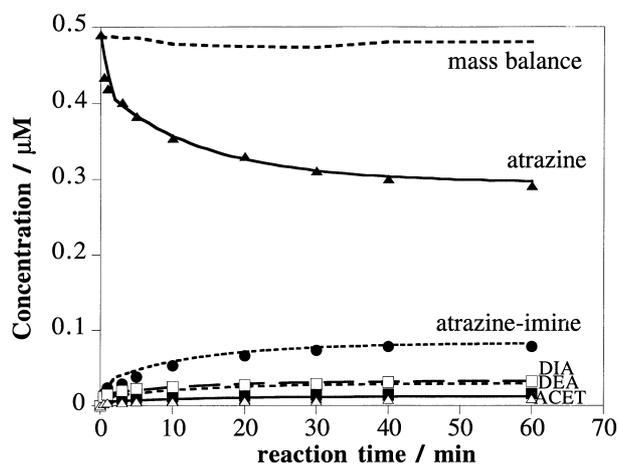


Fig. 8 Atrazine degradation and formation of metabolites during ozonation of lake Zürich water. Laboratory batch experiment at pH 8, 11 °C with an ozone dosage of 1 mg/L. DIA: deisopropyl-atrazine, DEA: deethyl-atrazine, ACET: atrazine-acetamide.

Our model predicts that atrazine is degraded by approximately 50% in the ozonation step without the gas-liquid transfer chamber. From laboratory experiments we know that an additional 10–15% degradation can be expected during the spontaneous ozone consumption phase. The modelled atrazine degradation is in agreement with preliminary measurements which have been done on the full-scale system. The atrazine concentration in the lake water was determined to be 6 ng/L. After the preozonation in the full-scale system 3.1 ng/L were found. Therefore, in the real ozonation reactor the degradation was in the same range as predicted by our model calculations. Thus, we have an independent tool to calibrate our model which allows to predict the degradation of any micropollutant as long as we know the corresponding rate constants for the ozone and OH radical reactions.

The oxidation of micropollutants during ozonation processes rarely leads to a mineralisation of these compounds. Usually in the treated water a mixture of metabolites can be expected which are products from the partial oxidation of the micropollutants. In the case of pesticides this is of particular importance, since these metabolites are also regulated in the new drinking water legislation of the EU [11]. For atrazine we have determined the most important metabolites for oxidation processes with ozone and OH radicals and the kinetics of the reactions of all metabolites with both oxidants. Figure 8 shows a laboratory batch ozonation of lake Zürich water which was spiked with atrazine (pH 8, 11 °C, ozone dosage 1 mg/L). The measured (symbols) and calculated (lines, calculated with R_{ct} -concept) atrazine concentrations are shown together with the measured and calculated formation of the main metabolites which are an atrazine-imine, an atrazine-acetamide, deethyl-atrazine and deisopropyl-atrazine [10].

It can be seen from Fig. 8 that the mass balance remains

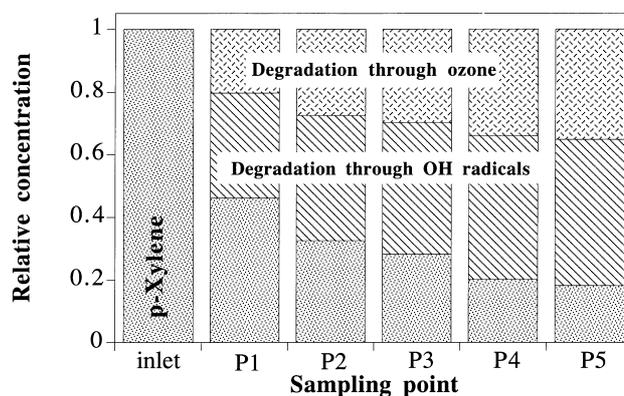


Fig. 9 Calculated degradation of p-xylene during ozonation in lake Zürich water ozonation reactor (pH 8, 5 °C; ozone dosage 1 mg/L).

constant for the entire ozonation even though atrazine is degraded by 40%. This means that in terms of the sum of atrazine and its metabolites the treated water has not improved its quality. From this laboratory study it can therefore be estimated that the main metabolites in the full-scale ozonation will be the same, because the degree of atrazine degradation has a similar extent in both systems. It has been further found in laboratory experiments that atrazine-imine hydrolyses to deethyl-atrazine with a half life of approximately 10 h at pH 8. Therefore, it can be expected that the end products (after 24 h) are mainly residual atrazine and deethyl-atrazine. This is consistent with many findings in the literature.

A further example for a degradation of a micropollutant (p-xylene) is shown in Fig. 9. The calculated relative concentration of p-xylene during full-scale ozonation of lake Zürich water in the reactor which was described earlier is depicted. p-xylene reacts both directly with ozone and with OH radicals with the corresponding second-order rate constants $k_{\text{O}_3, \text{p-xylene}} = 140/\text{M/s}$ [12] and $k_{\text{OH}, \text{p-xylene}} = 7 \times 10^9/\text{M/s}$ [13]. The rate constant for the oxidation by ozone lies in the medium range of possible rate constants for ozone reactions. Compared to atrazine oxidation it can be expected that a higher fraction of p-xylene is oxidised by molecular ozone. From Fig. 9 we learn that p-xylene is degraded down to 20% of its initial concentration. The degradation occurs to 35% by molecular ozone and 47% by OH radicals. In the case of atrazine, molecular ozone oxidation was of only minor importance.

CONCLUSIONS

We have shown that it is possible to combine laboratory experiments (characteristics of the oxidants in a particular water, kinetics of oxidation processes), hydraulics of reactors and reactive tracers to calibrate a full-scale ozonation system. As a result we can model disinfection (bacteria, virus, protozoa) and oxidation of organic micropollutants (e.g. fuel additives, pharmaceuticals, endocrine disrupters, etc.) if we know their reactivities towards ozone and OH radicals.

The combination of laboratory experiments with full-scale experiments by computer modelling shows that it is possible to predict ozone profiles, and OH radical reactions in a full-scale process. The behaviour of ozone can be directly derived from the decomposition kinetics in laboratory batch experiments where also the R_{ct} -value (ratio of OH radical concentration and ozone concentration) can be measured through the decrease of a probe compound. On a full-scale level these kinetics can be coupled with the hydraulics of the reactor. The ozone and OH radical reactions can then be tested by the use of reactive tracers such as ozone, chlorine and atrazine which are either added during routine operation of ozonation processes (ozone, chlorine) or are present in the raw water as undesired micropollutants (atrazine).

Our model which characterises ozonation reactors with respect to the overall oxidation capacity due to ozone and OH radicals will in the future be expanded to predict dynamic disinfection and bromate formation.

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