Advanced oxidation technologies for the degradation of pesticides in ground water and surface water

G.F. Ijpelaar*, M. Groenendijk**, R. Hopman* and Joop C. Kruithof***

* Kiwa N.V., Research and Consultancy, P.O. Box 1072, 3430 BB Nieuwegein, The Netherlands
** N.V. WNW Water Supply Company "North-West-Brabant", P.O. Box 3444, 4800 DK Breda, The Netherlands
*** N.V. PWN Water Supply Company North Holland, P.O. Box 2113, 1990 AC Velsenbroek, The Netherlands

Abstract An overview of the Advanced Oxidation Processes (AOP) studied for the degradation of pesticides combined with the formation of by-products is presented. It was found that the degree of conversion of pesticides is about the same with the Fenton process and UV/H2O2 within the margin of practical application, but slightly different with ozone/H2O2. Bentazone is readily degraded by the latter process, but more persistent during water treatment with the Fenton process and UV/H2O2, whilst atrazine is difficult to convert with all of these processes. Although bromate formation cannot be avoided completely with ozone/H2O2, it can be realized with the Fenton process and UV/H2O2. Upon degradation of pesticides with UV/H2O2, nitrite is produced, the amount depending on the water quality with respect to the nitrate concentration. Based on the a-selective nature of the hydroxyl radical AOC is formed out of DOC, which indicates that ozone/H2O2, the Fenton process as well as UV/H2O2 should be applicable for the development of biological GAC filtration.

Keywords AOP; bromate; Fenton process; ozone/H2O2; pesticides; UV/H2O2

Introduction

Since the early 1980s pesticides were found in raw water sources in The Netherlands. Initially they were only encountered in surface water, but in the last few years pesticides have also been present in ground water. This development triggered water supply companies to search for solutions for the removal/degradation of the pesticides in order to meet the Dutch standard of ≤ 0.1 µg/L per individual pesticide.

In general, removal of pesticides from water can be achieved by oxidation, GAC and membrane filtration. A disadvantage of the latter two methods is the relatively high costs if the process is only applied for pesticide control. The advantage of oxidation processes is the combination of disinfection and degradation of organic micropollutants. Disadvantages of oxidation are the formation of pesticide degradation products and other by-products. Optimization of the conditions with respect to the desired degree of degradation of micropollutants and by-product formation will make oxidation processes cost-effective.

Ozonation of raw water for the production of drinking water was already an accepted process worldwide for disinfection in the early 1980s and appeared in combination with Granular Activated Carbon filtration (GAC) also a successful barrier for pesticides. Although it was already known that bromate is formed during ozonation of bromide-containing water, it was in 1990 that Kurokawa and co-workers published results concerning the carcinogenic effects of bromate (Kurokawa et al., 1990). In order to limit the formation of bromate, research on ozone/H2O2 was started (Meijers et al., 1993). The current proposed standard for bromate in drinking water in The Netherlands without disinfection is ≤ 1.0 µg/L and ≤ 5.0 µg/L for disinfection purposes. In 1996 it was found that the Fenton process and UV/H2O2 should be considered promising processes for both pesticide and...
bromate control in anaerobic ground water and surface water, respectively. N.V. PWN Water Supply Company North Holland has started a large-scale test application on pesticide control with UV/H$_2$O$_2$ in 1997 (Kruithof et al., 1999). Since 1999, PWN is conducting research on UV disinfection (Kruithof et al., 2000).

Unlike ozonation, the ozone/H$_2$O$_2$ process is just like Fenton’s Reagent and UV/H$_2$O$_2$ mainly based on the formation of hydroxyl radicals. This gives the opportunity to compare these processes and also ozonation with respect to degradation of pesticides and formation of by-products (bromate, nitrite and AOC).

The objectives for the research on development of oxidation processes alternative to ozonation and ozone/H$_2$O$_2$ were pesticide control (ground water) and the combination of pesticide control and disinfection (surface water) without, or with limited, bromate formation.

The current research aims at optimization of these alternative processes concerning application of:
• pesticide control in anaerobic ground water with AOC and H$_2$O$_2$ removal based on sand filtration, which research has been started this year by WNWB Water Supply Company “North-West-Brabant” on location Waalwijk;
• pesticide control focussing at the nature and amount of AOC initiating biological GAC.

Theoretical background
The studied processes all rely mainly (ozone/H$_2$O$_2$ and UV/H$_2$O$_2$) or completely (Fenton process) on oxidation with hydroxyl radicals (OH·). The oxidation potential of OH· is 2.8 V compared to the 2.1 V of molecular ozone, which makes it possible to even degrade stable pollutants. Oxidation processes based on degradation with the hydroxyl radical are called Advanced Oxidation Processes (AOP), since the radicals are formed in-situ.

During reaction of ozone with H$_2$O$_2$ these radicals are formed by the reaction:

$$2O_3 + H_2O_2 \Rightarrow 2OH^- + 3O_2$$

The stoichiometric H$_2$O$_2$/O$_3$ ratio for the production of the radicals is 0.35 g/g. An optimal radical formation is realized at ratios between 0.5 and 1 g/g. For disinfection purposes an excess of ozone is applied: H$_2$O$_2$/O$_3$ ~ 0.2 g/g.

The principle of the Fenton process is the reaction between iron(II) and H$_2$O$_2$:

$$Fe^{2+} + H_2O_2 \Rightarrow Fe^{3+} + OH^- + OH.$$ 

Although this process is catalytic in iron at pH < 4, it can be applied at pH values up to 6.5. At pH < 4 a multiple production of OH· is achieved, while at pH > 4, as a result of hydroly-sation and precipitation of Fe$^{3+}$, only a single production of OH· takes place. This means that at pH 4–6.5 the rate of reduction of ferric iron back to ferrous iron by peroxide is still faster than the hydrolysation and precipitation of ferric iron as ferric hydroxide. At pH > 6.5, the production of OH· decreases significantly.

Upon treatment of peroxide-containing water with UV-C radiation OH· is homolytically formed out of H$_2$O$_2$:

$$H_2O_2 \overset{hv}{\rightarrow} 2OH^-$$

The coefficient of H$_2$O$_2$ for the absorption of UV radiation decreases with the wavelength, which indicates that the radical yield is reversely proportional with the wavelength.
Experimental set-up
The experimental part of the research on degradation of pesticides with ozone/H$_2$O$_2$ and the Fenton process is described in detail by Meijers et al. (1995) and Ijpelaar et al. (1998), respectively. Experiments of degradation of pesticides with UV/H$_2$O$_2$ were performed with two types of surface water (see Table 1). The water was passed through the quartz cell of the UV equipment at a flow of 1 liter per hour. The water and quartz cell were cooled with ultra-pure water. A mix of pesticides was added to each water type to a final concentration per pesticide of 0.5 µg/L. The UV doses were corrected for UV absorption by the quartz tube, quartz cell and cooling-water. Before and after the experiments, samples were taken for analysis on the pesticides, bromate and nitrite.

Results and discussion
Water treatment with ozone/H$_2$O$_2$

Degradation of pesticides. The efficiency with which the hydroxyl radicals are formed during reaction between ozone and H$_2$O$_2$ depends slightly on the pH of the water, but is rather independent of the temperature (5–25°C) and the H$_2$O$_2$ dose (H$_2$O$_2$/O$_3$ > 0.5 g/g). However, increasing the pH induces a change of the oxidation mechanism from mainly the molecular ozone pathway to mainly the radical and carbonate pathway. Raising the pH causes a significant increase in the reaction rate between ozone and H$_2$O$_2$. At pH 8 the reaction between these two components is complete within about 1 minute, while at a pH of 7 the time to complete this reaction is about ten minutes. Figure 1 shows the degradation of atrazine with ozone/H$_2$O$_2$ versus the ozone dosage at the pH values 7.5 and 8 (Meijers et al., 1995).

Table 1 Water quality on performance of the UV/H$_2$O$_2$ experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water type I</th>
<th>Water type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.5</td>
<td>7.8</td>
</tr>
<tr>
<td>Turbidity (FTU)</td>
<td>4.2</td>
<td>0.31</td>
</tr>
<tr>
<td>Bromide (µg/l)</td>
<td>103</td>
<td>204</td>
</tr>
<tr>
<td>Bromate (µg/l)</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Nitrate (mg/l)</td>
<td>2.3</td>
<td>9.3</td>
</tr>
<tr>
<td>Nitrite (mg/l)</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>NPOC (mg C/l)</td>
<td>2.4</td>
<td>3.5</td>
</tr>
<tr>
<td>AOC (µg Acetate-C/l)</td>
<td>11</td>
<td>37</td>
</tr>
</tbody>
</table>

$^1$ NPOC: non-purgable organic carbon

Figure 1 Effect of the pH on the degradation of atrazine by ozone/H$_2$O$_2$ (H$_2$O$_2$/O$_3$: 0.5–2.5 g/g, DOC = 2.3 mg C/L and T = 5°C)
Duguet et al. (1990) found that the conversion of atrazine is mainly due to reaction with hydroxyl radicals rather than through ozonation. The slightly higher degree of conversion of atrazine at elevated pH and H$_2$O$_2$/O$_3$ ratios may therefore be attributed to the reaction of the hydroxyl radicals with H$_2$O$_2$ and other scavenging compounds and ions present (e.g. carbonate and DOC). However, the more easily degradable a pesticide is, the larger the difference in degree of degradation upon changing the pH and H$_2$O$_2$/O$_3$ ratio (see Figure 2). Compared to atrazine, isoproturon and 2,4-D are relatively easy degradable, whilst dikegulac is a more persistent pesticide (Ijpelaar et al., 1998).

Bromate formation. During oxidative treatment of bromide-containing water with ozone based processes bromate formation may occur. A standard for the presence of bromate in drinking water and renewed analysis methods brought about a review of the applied processes. Although bromate is formed by the molecular ozone pathway as well as the hydroxyl radical pathway, the extent to which it is formed may be limited by optimization of the H$_2$O$_2$/O$_3$ ratio (see Figure 3).

In the presence of sufficient H$_2$O$_2$, a shift of the oxidant from ozone to the hydroxyl radical takes place. Based on the radical pathway bromide is oxidized to bromate through formation of hypobromite (·OBr) which is subsequently reduced by H$_2$O$_2$ to bromide (Gunten and Oliveras, 1997). However, bromate formation cannot be excluded completely since reaction between ozone and bromide will always proceed to a certain degree. Besides
optimization of the H$_2$O$_2$/O$_3$ ratio, also the pH, temperature and mass transfer play a role in the amount of bromate produced. These three parameters all minimize the concentration of the effective ozone concentration for the formation of bromate. The pH has a significant effect on the reaction rate between ozone and H$_2$O$_2$ since it is proportional with the OH$^-$ concentration of the water. Increasing the pH by one unit will bring about a tenfold increase of the reaction rate. So, application of an excess of H$_2$O$_2$ will restrict the effective ozone concentration in the bulk of the solution, while there is still sufficiently H$_2$O$_2$ left for the reduction of the hypobromite radical in the bromate formation process. The temperature is reversely proportional to the solubility of ozone in water, indicating that bromate formation may increase on reduction of the temperature. Minimizing the mass transfer from ozone from the gas phase to the water phase may reduce the reaction between ozone and bromide at the bubble surface. This may be brought about by decreasing the ozone concentration in the gas and increasing the bubble size (Meijers et al., 1998).

**Pesticide control in anaerobic ground water with the Fenton process**

*Degradation of pesticides.* The Fenton process, commonly used for the treatment of waste water is commonly carried out on water with pH values near 3. Under these optimal conditions the process has proven to be an excellent method for the degradation of organic micropollutants (Pignatello, 1992). However, this does not mean that an effective degradation of micropollutants cannot be achieved at a “less optimal” condition as a realistic pH of anaerobic ground water (see theoretical background). Figure 4 shows the degradation of some pesticides versus the pH of the treated water.

Figure 5a shows the degradation of atrazine and 2,4-D at an initial pH of 6. It can be seen that atrazine, which is commonly used as a model pesticide, is degraded for more than 70% within a 1 minute contact time. Based on AOP, the pesticide 2,4-D can be converted for more than 98% in less than half a minute. About the same results have been achieved on application of ozonation and the combination of O$_3$ and H$_2$O$_2$.

Besides the pH, the oxygen concentration of the water and the H$_2$O$_2$ dose also play a decisive role. The rate of oxidation of iron(II) with oxygen at near neutral pH is much higher than the rate of reaction between iron(II) and hydrogen peroxide. This means that the oxygen content of the water has to be very low (0–0.3 mg/l depending on the iron(II) concentration) on application of the Fenton process for ground water treatment. Figure 5b shows the degradation of atrazine at pH 6 in the presence of oxygen.

*Pesticide control and bromate formation vs. H$_2$O$_2$ dose.* Figure 6 presents the degradation of some chlorophenoxy pesticides as a function of the H$_2$O$_2$ dose.

![Figure 4](https://iwaponline.com/ws/article-pdf/2/1/129/408563/129.pdf) Degradation of pesticides versus the pH: atrazine (.), isoproturon (.), linuron (□), and diuron (o)
The degradation of micropollutants is determined to a large extent by the applied H2O2 dose. Based on the formation of bromate, this parameter becomes critical near the stoichiometric point with respect to the iron(II) concentration. During degradation of the pesticides bromate can be produced by parallel oxidation of bromide by hydroxyl radicals. In excess H2O2, the formation of bromate can be prevented (see Water treatment with ozone/H2O2). However, dosing a short measure of H2O2 to the anaerobic ground water of Waalwijk (WNWB) did not result in the formation of bromate (< 0.2 µg/L). This is probably the result of the low Br-/DOC ratio. Since Dissolved Organic Carbon (DOC) may be considered one of the largest scavengers of hydroxyl radicals, a low Br-/DOC ratio (Waalwijk: 0.02) combined with a low H2O2 dose may prevent bromate formation.

**Fenton process in practice.** The above results show that application of the Fenton process for degradation of organic micropollutants in conventional ground water treatment plants should occur before the anaerobic water is aerated, keeping in mind a maximum pH of 6.5 and a contact time of about one minute. Furthermore, the H2O2 concentration of the water after reaction has to be low as the presence of H2O2 in a Rapid Sand Filter (RSF) may dissolve deposited manganese dioxide. Current research at the ground water plant Waalwijk (WNWB) aims at the application of the Fenton process with respect to the biological processes in RSF (especially the nitrification) and removal of AOC and remaining concentrations of H2O2 by rapid-sand filtration.
Since, in general, ground water does not have to be disinfected, it offers the possibility of application of a cheap process. Apart from rebuilding an existing ground water treatment plant, the process costs of the Fenton process are based on dosage of H\textsubscript{2}O\textsubscript{2} which comprises about 0.007 US$/m\textsuperscript{3} water for the treatment with 5 mg/L H\textsubscript{2}O\textsubscript{2}. According to current knowledge, in practice the Fenton process should be applied prior to aeration:

**Pesticide control in surface water with UV/H\textsubscript{2}O\textsubscript{2}**

*Degradation of pesticides.* Pesticides can be degraded effectively with the combination of UV radiation and hydrogen peroxide (UV/H\textsubscript{2}O\textsubscript{2}). The fact that this process also possesses disinfection capacity makes it applicable for surface water treatment.

Figure 7 present the results of degradation of a series of selected pesticides in different surface waters with UV/H\textsubscript{2}O\textsubscript{2}. It can be seen that more than 80% conversion can be realised. Moreover, a discrepancy between degradation of the pesticides exists based on the oxidation regime. This indicates that the real degree of conversion can be adjusted based on the UV and H\textsubscript{2}O\textsubscript{2} dose. Since easily degradable pesticides are already converted at relatively low doses, this counts mainly for the less easily degradable pesticides, like atrazine and bentazone. Concentrations of pesticides in practice exceeding the standard of ≤ 0.1 µg/L are generally in the range 0.1–0.2 µg/L. This implies that a 50% degradation of these pesticides is sufficient to make sure that the obtained concentrations follow the Dutch Directive for distribution of water qualities. Pesticides like mecoprop (MCPP) and MCPA are degraded for more than 90% on application of a UV dose of 1000 mJ/cm\textsuperscript{2} (13 mg/L H\textsubscript{2}O\textsubscript{2}). However, a 90% conversion of atrazine and bentazone in the concerning surface water takes a UV dose of about 3,000 mJ/cm\textsuperscript{2}.

The degradation of the pesticides in the two investigated surface waters is comparable, in spite of the significant difference in water quality. Although different H\textsubscript{2}O\textsubscript{2} concentrations were applied, atrazine was found to be converted between about 45 and 55% using a UV dose of 1,000 mJ/cm\textsuperscript{2}. This is remarkable since especially the turbidity and the nitrate and NPOC concentrations play a dominant role when using UV technology and Advanced Oxidation Processes (AOP). A high turbidity decreases the transmission of the water which may result in a too low UV dose in the reactor at high distances from the lamp. Nitrate absorbs photons strongly (see below) whilst organic species (NPOC) are considered a strong scavenger of hydroxyl radicals.

*By-product formation.* As is the case with oxidation of raw water with ozone/H\textsubscript{2}O\textsubscript{2} and the Fenton process, bromate formation can be avoided on application of an excess of H\textsubscript{2}O\textsubscript{2} (see above). All experiments with UV/H\textsubscript{2}O\textsubscript{2} were performed with (slight) excess of H\textsubscript{2}O\textsubscript{2}, which resulted in no formation bromate throughout this research or limited to a concentration of < 0.2 µg/L (detection limit).
Nitrite, which is a product of reduction of nitrate, cannot be formed by reaction of nitrate with \( H_2O_2 \) or \( OH^- \). It is instead produced by absorption of photons by nitrate which results in cleavage of one of the nitrogen-oxygen bonds. The energy needed for this cleavage corresponds with UV radiation of < 240 nm wavelength (Von Sonntag et al., 1992). Since \( H_2O_2 \) is homolytically cleaved by UV radiation of the same wavelength, nitrate should be considered a competitor of \( H_2O_2 \) towards absorption of the photons. This implies that in case of water treatment containing high nitrate levels high \( H_2O_2 \) doses are needed both for the production of a sufficient amount of hydroxyl radicals and to limit the formation of nitrite. Moreover, it suggests that, in order to limit the nitrite production, water containing relatively easy degradable pesticides but with a high nitrate concentration may be treated with a soft oxidation regime based on UV radiation with a wavelength > 240 nm. The formation of nitrite which followed from this research is presented in Figure 8. It shows on the one hand that the concentration of nitrite increases strongly raising the UV dose. On the other hand it is clear that less nitrite is produced if the \( H_2O_2 \) dose is increased. It was found that the amount of nitrite formed at the applied conditions is much higher than the current standard in The Netherlands for drinking water which is 0.1 mg/l \( NO_2^- \). It is, however, questionable how much effort should be put in limiting the nitrite formation, since it may be expected that nitrite will be oxidized back to nitrate relatively easily during GAC filtration.

**Practical application of UV/\( H_2O_2 \).** Application of UV/\( H_2O_2 \) for the degradation of organic micropollutants is less cheap than the Fenton process which is mainly the result of the electrical costs of production of ultraviolet radiation. These costs correspond simply with the
applied UV dose, which makes oxidation with UV/H₂O₂ about twenty times more expensive than UV disinfection. Strictly based on the UV and H₂O₂ dose for 80% degradation of pesticides, the process costs of UV/H₂O₂ are about 0.06 US$/m³ water. Cost efficiency could be obtained by application of UV technology for disinfection as well as oxidation. As mentioned above, the current method of AOC and H₂O₂ removal is GAC filtration. In water treatment plants UV technology would probably be fit as follows:

AOC formation during water treatment with Advanced Oxidation Processes
Besides bromate, Assimilable Organic Carbon (AOC) is also produced during oxidative treatment of raw water. This is due to reaction of .OH with Natural Organic Matter (NOM, among which is DOC) resulting in assimilable organic carbon which can easily be consumed by bacteria. Since this may cause regrowth of bacteria in the water distribution system, it has to be removed a priori. The proposed standard of AOC in drinking water in The Netherlands is 10 µg Acetate-C/L. This value is based on distribution of the water without the presence of a secondary disinfectant.

The results of AOC formation during various water treatment conditions with the Fenton process are shown in Figure 9.

The unexpectedly high value of AOC during degradation of the pesticides at a H₂O₂ dose of 2.2 mg/l is most probably caused by infection during the lab-scale experiment.

The current state-of-the-art removal of AOC and H₂O₂ remaining after oxidation is by using granular activated carbon (GAC). The H₂O₂ is thereby converted into oxygen whilst AOC is consumed by bacteria living on the carbon. The latter process forms the base for development of a biologically GAC filtration. Although this research did not aim to
develop an oxidation process which can be used as a source of easy assimilable organic carbon, it will be investigated in future research.

Conclusions

Atrazine and bentazone are the most persistent pesticides based on treatment with hydroxyl radicals. However, bentazone is relatively easily degraded on application of ozone/H₂O₂, which discrepancy is due to the additional degradation by molecular ozone. As described above, atrazine is converted completely by reaction with OH• which may result in a poor degradation of atrazine with ozone/H₂O₂ if the H₂O₂/O₃ ratio is not optimal. Pesticides like mecoprop and MCPA are converted readily with all three processes.

To control pesticides in surface water containing high levels of bromide, the UV/H₂O₂ oxidation process is preferred above ozone/H₂O₂. If the primary processes in the sand filters are not disturbed on application of H₂O₂, the Fenton process is very cost-effective for pesticide control in anaerobic ground water. In contrast with ozone/H₂O₂, bromate formation can be avoided with both the Fenton process and UV/H₂O₂. Upon irradiation of water with high levels of nitrate, nitrite is formed. This can be controlled by optimization of the H₂O₂ dose with respect to the nitrate concentration.

Since all studied oxidation processes rely mainly or completely on oxidation by hydroxyl radicals, AOC formation occurs by reaction with DOC. The amount of AOC formed with the Fenton process depends on the applied H₂O₂ dose. Under the conditions of this research, between 10 and 60 µg Acetate-C/L was formed.

References


