Fenton process for the combined removal of iron and organic micropollutants in groundwater treatment

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Abstract Fenton process, known as Advanced Oxidation Process for the degradation of organic pollutants in waste and drinking water, was studied for the combination of iron removal and pesticide control in anaerobic groundwater. The combined effect of aeration and rapid sand filtration, which are commonly applied in groundwater treatment, was studied in a pilot plant. Pesticide degradation was performed on laboratory scale. It was found that addition of 2 mg/L H₂O₂ prior to aeration improved the removal of iron without hindering the filtration processes of manganese removal and nitrification. Under these conditions, the laboratory-scale tests showed pesticide degradations of up to 80% (influent concentration 1.6–2.5 µg/L). Dosing 8.5 mg/L H₂O₂ all selected pesticides were converted more than 80%. However, this dose appeared to have an adverse effect on the removal of iron and manganese and the nitrification process. This is attributed to the presence of relatively high concentrations H₂O₂ in the water entering the rapid sand filter. By filtration AOC, formed during oxidation with the low H₂O₂ dose, was reduced from about 70 µg/L to about 15–20 µg Acetate-C/L. Bromate formation did not occur. Residual H₂O₂ varied from 0.1–0.2 mg/L (2 mg/L H₂O₂ dose) to 0.2–0.4 mg/L (8.5 mg/L H₂O₂ dose) which is higher than the proposed guideline of 0.019 mg/L.

Keywords AOC; bromate; Fenton process; iron; manganese; oxidation; pesticides

Introduction

In The Netherlands about 225 groundwater treatment plants are currently in use for the production of drinking water. This corresponds with about 60% of the total drinking water production. Groundwater treatment plants in The Netherlands are based on oxidation-filtration using aeration followed by rapid sand filtration. The treatment includes in general the removal of iron, manganese, ammonium, and methane and in some cases hydrogen sulfide. The standard for iron in drinking water in the Netherlands is <0.05 mg/L. In order to reduce the flushing costs of distribution systems many water supply companies aim to reduce the iron content to <0.03 mg/L. However, iron is not always sufficiently removed from groundwater. Because since the early nineties of the last century pesticides have been found in groundwater, several Dutch plants are also equipped with granular activated-carbon (GAC) filters in order to comply with the European standard of <0.1 µg/L per pesticide in drinking water (Somiya et al., 1986; Van der Hoek et al., 1995). Most of the pesticides are removed well by GAC filtration, except strongly polar compounds like glyphosate and AMPA (Hopman et al., 1995). Since GAC filtration is also rather expensive, water supply companies would be served with a cheap and effective method for the removal of pesticides from groundwater and, if necessary, improvement of the iron removal as well.
In general, the advantage of oxidation processes may be the combination of disinfection and degradation of organic micropollutants. However, application of ozone and ozone/H₂O₂, intensively studied since the late eighties, results in bromate formation if applied to bromide-containing waters (Kruithof et al., 1996). In 1996 it was concluded that the Fenton process should be considered a promising method for both pesticide and bromate control in anaerobic groundwater (Ijpelaar, 1997). Moreover, during the Fenton process Fe(II) is oxidized to Fe(III) which may support the removal of iron from groundwater.

This paper describes the results of the research examining the Fenton process for improvement of iron removal and degradation of pesticides in anaerobic groundwater. The study was based on a conventional groundwater treatment without the implementation of an additional filtration step. This was performed in collaboration with the WNWB Water Supply Company “North-West-Brabant” with groundwater from water treatment plant Waalwijk. The impact of a low (2 mg/L) and a high (8.5 mg/L) hydrogen peroxide dose on the processes of both manganese removal and nitrification and the formation and removal of oxidation by-products (bromate, AOC) are discussed as well.

**Theoretical background Fenton process**

About a century ago Fenton reported the oxidation of maleic acid by Fe(II)/H₂O₂, the so-called Fenton’s Reagent (Fenton, 1884). The oxidizing agent, the hydroxyl radical, is produced according to the following reaction

Fe(II) + H₂O₂ ⇌ Fe(III) + OH⁻ + ·OH (1)

Among others Fenton’s reagent is employed for the treatment of phenolic wastes. In addition, the potential for the degradation of a/o pentachlorophenol (Faust, 1994) and 2,4-D (Pignatello, 1992) has been established. In reaction (1) Fe(III) is produced which enables the decomposition of H₂O₂ catalytically hereby generating hydroxyl radicals (Walling, 1975).

Fe(III) + H₂O₂ ⇌ Fe-OOH²⁻ + H⁺ (2)

Fe-OOH²⁻ ⇌ Fe(II) + HO₂⁻ (3)

Fe(II) + H₂O₂ ⇌ Fe(III) + OH⁻ + ·OH (1)

This process, the Fenton-like reagent, is believed to be the major mechanism in wastewater applications.

The system has its maximum catalytic effect at a pH of 2.8–3.0. At low pH reaction (2) is inhibited, at high pH Fe(OH)₃ precipitation takes place. Therefore, Fe(III) chelates are used to convert high concentrations of herbicides and pesticides at neutral pH (Sun and Pignatello, 1992). For degradation of high pesticide concentrations in wastewater this approach is necessary to restrict iron concentration and reaction time. For drinking water treatment with a restricted pesticide degradation of just a few tenths of micrograms per litre another approach may be possible. The required pesticide degradation may be achieved by the Fe(II) concentration present in the groundwater and ambient pH. Since at ambient pH Fe(III) is hydrolyzed instantaneously, this approach is based on a single production of hydroxyl radicals.

To enable an optimal production of radicals by the reaction between Fe(II) and H₂O₂, the presence of oxygen should be prevented. Therefore, addition of hydrogen peroxide should take place prior to aeration, taking into account the required contact time.
Materials and methods

All experiments besides those on degradation of pesticides were performed on location Waalwijk. For this purpose a pilot plant was used consisting of an aeration step followed by rapid sand filtration. During two periods of two weeks, hydrogen peroxide in concentrations of 2 or 8.5 mg/L was dosed to the anaerobic water prior to aeration. The experiments on degradation of the pesticides mecoprop (MCPP), dicamba, 2,4-DP and bentazone at a concentration of about 2 µg/L were performed in a laboratory and are described in detail by Ijpelaar et al., 2000. During these experiments the groundwater from Waalwijk was kept under a nitrogen atmosphere. The applied hydrogen peroxide doses were 2.1, 4.3, 6.3 and 9 mg/L. After reaction times of 5, 3, 2 and 1.5 minutes respectively, sodium sulfite was dosed to quench the Fenton process and samples for analysis on the pesticides, bromate and AOC were taken.

Fenton process for the removal of pesticides

Degradation of pesticides

Figure 1 presents the degradation of some chlorophenoxy pesticides and bentazone as a function of the H$_2$O$_2$ dose at pH 6.5. Furthermore, the bromate content of the water after oxidation with the Fenton process is given.

It shows that the degree of degradation of the pesticides varies much with the applied H$_2$O$_2$ dose. It is expected that the formation of hydroxyl radicals (·OH) is limited at low H$_2$O$_2$ doses. This effect may become severe if radical formation is the rate-determining step in the degradation of the pesticides. Furthermore, it can be seen that the hydroxyl radical, being responsible for the degradation of the pesticides, may be not completely aselective, even for pesticides within the same class. This is most strongly revealed at the lowest H$_2$O$_2$ dose. Mecoprop being the easiest to convert was degraded between >70% to nearly >98% at an elevated H$_2$O$_2$ dose. Although only about 40% of the initial dicamba concentration is reduced on addition of 2 mg/L H$_2$O$_2$, more than 95% is degraded using about 8.5 mg/L H$_2$O$_2$.

Table 1 Characteristics of the raw water from groundwater treatment plant Waalwijk

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>7.5</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
</tr>
<tr>
<td>HCO$_3$–</td>
<td>205</td>
</tr>
<tr>
<td>Br–</td>
<td>0.08</td>
</tr>
<tr>
<td>DOC (as NPOC)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 1 Degradation of pesticides and formation of bromate versus the H$_2$O$_2$ dose at pH 6.5. The reaction times were as given in the materials and methods section.
Bromate formation

Bromate concentrations found after oxidative treatment of the groundwater were lower than the detection limit of 0.2 µg/L (see Figure 1). It is well known that oxidation of bromide-containing water may cause production of bromate. This counts in particular for ozonation of such waters, but hydroxyl radicals may also form bromate out of bromide. This process involves a series of reactions in which the OBr⁻/HOBr (with ozone) and ·OBr (with ·OH) are the most important intermediates (von Gunten et al., 1997). These intermediates are reconverted to bromide by hydrogen peroxide. From this it can be concluded that formation of bromate by the Fenton process will not occur. If there is enough H₂O₂ left besides that necessary for the reaction with Fe(II), the hydroxyl pathway will not proceed beyond the formation of the ·OBr radical. If the molar concentration of H₂O₂ is lower than the molar Fe(II) concentration as in reaction (1), hydroxyl radical formation will stop on exhaustion of the H₂O₂ dose thereby avoiding bromate formation.

Effect of hydrogen peroxide on groundwater treatment

Iron removal and turbidity

Figure 2a presents the concentration of iron after oxidation and filtration of the groundwater (pH 6.5). The oxidation step consisted of H₂O₂ dosage (2 and 8.5 mg/L) followed by aeration.

These results show that the filtrate iron concentration is lowered from about 0.1 mg/L to <0.01 mg/L (detection limit) as a result of the presence of 2 mg/L H₂O₂, dosed to the anaerobic groundwater. Increasing the H₂O₂ dose to 8.5 mg/L led to an iron concentration in the filtrate comparable to the iron content of the water prior to dosing H₂O₂.

Theoretically, for the decomposition of 2 mg/L H₂O₂ only about half of the Fe(II) content of the raw groundwater is needed. This means that under these conditions the Fenton process should proceed leaving no or a low H₂O₂ residual. This is however not the case for a H₂O₂ dose of 8.5 mg/L. At the end of the Fenton process, using the higher H₂O₂ concentration, a significant H₂O₂ residual is still present in the water entering the rapid sand filter. Since Fe(III) species at pH 6–7 can be reduced by H₂O₂ to Fe(II), the iron content of the filtrate may be the result of this effect. In spite of the buffer capacity of the groundwater of Waalwijk, it was found that the pH after dosage of 9 mg/L H₂O₂ was lowered from 6.5 to 6.0. Moreover, earlier research with the same groundwater revealed a pH-drop from 6 to pH 4.5. Since the pH of the water during filtration is not known, further research is necessary to reveal the mechanisms involved.

The same pattern as found for the hydrogen peroxide-induced iron removal in Figure 2a was realized for the filtrate turbidity of the rapid sand filter (see Figure 2b). This supports the mechanism described above that the 2 mg/L H₂O₂ dosed is mainly or completely utilized for the Fenton process, realizing an improved iron removal. As said, on application of 8.5 mg/L H₂O₂, it is expected that soluble and insoluble Fe(III) species deposited in the

Figure 2 (a) Iron content of the raw water (Δ), after oxidation (●) and after filtration (●) and (b) filtrate turbidity versus time. The H₂O₂ doses and periods are given in the graphs.
rapid sand filter are reduced. This may result in the formation of iron colloids, which are measured as an increased turbidity.

**Removal of manganese**

Manganese removal from groundwater may, besides the chemical pathway, occur biologically (Ghiorse, 1984). Taking this into account, the presence of hydrogen peroxide may affect both the chemical and the biological manganese removal. A comparison between both mechanisms will however not be dealt with in this paper.

Chemically, manganese ions are oxidized by oxygen to the thermodynamically less stable $\text{Mn}_3\text{O}_4$ before oxidizing to $\text{MnO}_2$. During this process, $\text{Mn}_3\text{O}_4$ acts as a catalyst (Graveland, 1971). Figure 3 shows the filtrate manganese concentration starting with no $\text{H}_2\text{O}_2$ followed by dosage of 2 and 8.5 mg/L $\text{H}_2\text{O}_2$ prior to aeration.

Apparently, a 2 mg/L $\text{H}_2\text{O}_2$ dose prior to aeration and filtration appeared to have no noticeable effect on the process of manganese removal under the applied conditions. This may be due to the low $\text{H}_2\text{O}_2$ content of the water entering the rapid sand filter resulting in a reduction reaction which is kinetically slow compared to the rate of reduction of Fe(III) species.

Figure 3 also shows that the filtrate manganese concentration during addition of 8.5 mg/L H$_2$O$_2$ is elevated to about 1.5 mg/L, which is a factor of 5 above the manganese content of the raw water. Hydrogen peroxide is thermodynamically capable of reducing MnO$_2$ to Mn$^{2+}$ chemically. It is therefore expected that above a certain H$_2$O$_2$ concentration, MnO$_2$, earlier deposited on the filter grains, will be reduced to soluble manganese significantly. The manganese concentration after the sharp rise to 1.5 mg/L is probably establishing equilibrium.

**Nitrification – removal of ammonium**

Removal of ammonium ions in rapid sand filters is achieved by nitrification, which results in the formation of nitrite ions. Subsequently, the nitrite ions are further oxidized to nitrate ions. These processes are achieved by the Nitrosomonas and Nitrobacter bacteria respectively:

$$\text{NH}_4^+ + 1.5\text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{NO}_2^- + 2\text{H}_3\text{O}^+ + 66 \text{ kcal} \quad (4)$$

$$\text{NO}_2^- + 0.5\text{O}_2 \Rightarrow \text{NO}_3^- + 17 \text{ kcal} \quad (5)$$
Figure 4a presents the effect of injection of the low and high H$_2$O$_2$ dose on the process of ammonium removal compared to no addition of H$_2$O$_2$.

As found with manganese removal, no adverse effect has been found on the removal of ammonium on addition of 2 mg/L H$_2$O$_2$ prior to aeration. The hydrogen peroxide content of the water in the rapid sand filter is apparently too low to cause any significant damage to the bacteria. Again, as found with the removal of iron and manganese, addition of 8.5 mg/L H$_2$O$_2$ has a negative impact on the nitrification process. Since it is not clear from these results how H$_2$O$_2$ reduces the effectiveness of this biological process, further research is needed.

Conversion of nitrite to nitrate
Figure 4b shows the changes in nitrite and nitrate content of the filtrate upon dosage of hydrogen peroxide. The course that the nitrite and nitrate concentration follows supports the effect which hydrogen peroxide has on the removal of ammonium. Based on the nitrite concentration, it can be concluded from Figure 4b that the Nitrobacter bacteria are not hindered by the presence of a low concentration of hydrogen peroxide: [NO$_2^-$] <0.01 mg/L. The filtrate nitrate concentration during this period is according to expectations.

Although based on just one datapoint, the increase of the nitrite content of the filtrate to about 0.2 mg/L dosing 8.5 mg/L H$_2$O$_2$ is a logical continuation on the decreased conversion of NH$_4^+$. As less nitrite is oxidized to nitrate, a reduced nitrate concentration in the filtrate is the consequence.

Formation of easily assimilable organic carbon (AOC)
During Advanced Oxidation Processes (AOP) AOC is predominantly produced by reaction of the hydroxyl radicals with dissolved organic carbon (DOC). The radicals may attack double bonds as well as functional groups, which results in carbon chains easily assimilable for bacteria. The amount of AOC produced by the Fenton process and present in the water after filtration can be found in Figure 5a. During the first 2-week period of H$_2$O$_2$ injection, e.g. 2 mg/L H$_2$O$_2$, an average of about 70 µg/L AOC (expressed as acetate-carbon) was formed. This value corresponds in order of magnitude with earlier measured AOC data during ozonation (Van der Hoek, 1995). Based on earlier studies on the removal of AOC during rapid sand filtration, the decrease from 70 to about 20 µg/L AOC is expected (Hijnen et al., 1999). This also counts for the further decrease to about 15 µg/L AOC as the filter performance for AOC removal improves with time in use.

No explanation was found for the significantly lower level of AOC formation when a H$_2$O$_2$ dose of 8.5 mg/L is applied. It is expected that the rate of hydroxyl radical formation increases with increasing H$_2$O$_2$ dose and that, therefore, within a certain period of time more AOC would be formed.
The concentrations of H$_2$O$_2$ at the end of the Fenton process but prior to aeration on the one hand and after filtration on the other are presented by Figure 5b. During addition of 2 mg/L H$_2$O$_2$ about 0.7 mg/L H$_2$O$_2$ was measured in the water after oxidation, while a 5 mg/L H$_2$O$_2$ residual was found after oxidation with 8.5 mg/L H$_2$O$_2$. The fact that a H$_2$O$_2$ residual is found using 2 mg/L H$_2$O$_2$ compared with a consumption of 3.5 mg/L on application of 8.5 mg/L is unclear.

It was found that during the period of research hydrogen peroxide was converted to a high extent during rapid sand filtration. It is expected that the processes described in this paper mainly cause the reduction in H$_2$O$_2$ concentration during filtration.

Although there exists no standard for the presence of hydrogen peroxide in drinking water, the amounts measured in the filtrate (0.1–0.4 mg/L) are probably not acceptable. This is based on a publication by the AWWA Research Foundation in which a maximum H$_2$O$_2$ concentration of 0.019 mg/L was reported at a risk level of 10$^{-6}$ (Bull and Kopfler, 1991).

Conclusions
The Fenton process for the combined removal of iron and pesticides is best applied on anaerobic groundwater with pesticide concentrations just exceeding the standard. This means that a low H$_2$O$_2$ dose may be sufficient to realize the desired level of iron and pesticide removal without the need of an additional filtration step for AOC removal. The research described in this paper did not deal with the combined removal of iron and pesticides, since the experiments were performed separately. However, it is unlikely that the process of iron removal by addition of hydrogen peroxide and the Fenton process for the degradation of pesticides will affect one another. Only the degradation of pesticides is based on the reaction between Fe(II) and H$_2$O$_2$. The improved iron removal is in fact a side effect of this reaction realizing a more complete oxidation of the available iron. From the results of this research the following conclusions have been drawn.

- The iron content of the rapid sand filtrate decreased from about 0.1 mg/L to <0.01 mg/L dosing 2 mg/L H$_2$O$_2$ prior to aeration. The same pattern was found for the turbidity of the water.
- Initial concentrations of <0.35 µg/L mecoprop, <0.16 µg/L dicamba, <0.26 µg/L 2,4-DP and <0.18 µg/L bentazone can be reduced to <0.1 µg/L using 2 mg/L H$_2$O$_2$. The degree of degradation varied between 40 and 80%.
- A residual 0.7 mg/L H$_2$O$_2$ entering the rapid sand filter did not adversely affect the other filtration processes, e.g. manganese removal and nitrification compared to no H$_2$O$_2$ dose.
A H$_2$O$_2$ residual of 5 mg/L (8.5 mg/L dose) appeared to have a negative effect on all filtration processes. Although it is expected that Fe(II) is oxidized to Fe(III) in good yield during the Fenton process, the subsequently produced Fe(III) species have probably been reduced in the filter by residual H$_2$O$_2$. This resulted in filtrate concentrations of 0.1–0.15 mg/L iron, 1–1.5 mg/L manganese, 0.1–0.2 mg/L ammonium and 0.2 mg/L nitrite.

The AOC concentration of 70 µg Acetate-C/L formed after oxidation with 2 mg/L H$_2$O$_2$ was lowered to about 15–20 µg/L after rapid sand filtration.

Bromate formation by oxidation of bromide did not occur either because of the presence of an excess of H$_2$O$_2$ to reduce the ·OBr intermediate or because hydroxyl radicals responsible for the formation of bromate were not available.

Filtrate H$_2$O$_2$ residuals were 0.1–0.2 mg/L and 0.2–0.4 mg/L using 2 and 8.5 mg/L H$_2$O$_2$, resp.

References