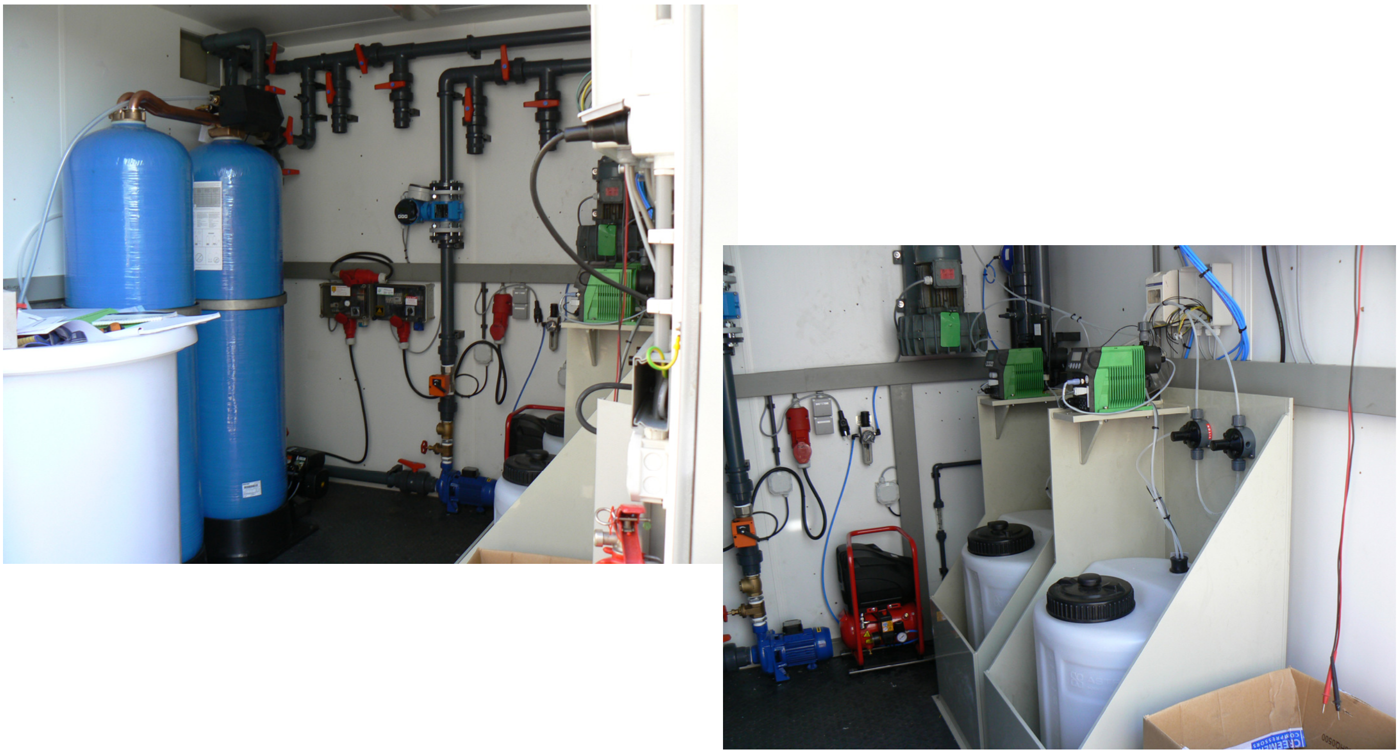

Fenton process for Contaminant Control

Investigation of OH radical formation with two water types

BTO 2008.051
December 2008

KWR Watercycle Research Institute

BTO

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This report has been distributed among BTO-participants and is publicly available.

Preface

This report is the result of the joint effort of KWR and Oasen in the BTO-project “removal of organic micropollutants from groundwater” (B111636) in 2007. The pilot facilities were built and operated by Oasen at water production site Kamerik. We especially would like to thank Ruud Kolpa and Petra Lafeber for their input and cooperation.

Unfortunately, the results with the Fenton process were negative at Kamerik. To check whether the methods were correctly chosen and experiments were carried out in the right way, additional work at water production site Waalwijk of Brabant Water was carried out. Stephan van de Wetering (Brabant Water) facilitated.

Furthermore, we would like to acknowledge the TECHNEAU project for (partly) funding this project. TECHNEAU is an Integrated Project Funded by the European Commission under the Sustainable Development, Global Change and Ecosystems Thematic Priority Area, contract number 018320.
And a special thanks to Ioannis Katsoyannis of EAWAG – one of the partners in the TECHNEAU project – who reviewed this report and gave valuable suggestions for improvement.

Summary

The advanced oxidation processes (AOP) are a technology which is applied to the drinking water treatment practice. One of these techniques is Fenton oxidation process using combination of hydrogen peroxide and ferrous iron to produce OH radicals which can oxidize organic compounds.

The Fenton process can be an effective way of water treatment, to remove micropollutants without bromate formation and with respect to the costs. So this investigation is about the possibilities of the Fenton process as AOP on some selected waters.

For this purpose, the Fenton process efficiency was investigated with two different types of anaerobic groundwater which came from two water treatment sites. The water types from Brabant Water (BW; Waalwijk) and Oasen (De Hooge Boom, Kamerik) were tested. The water of Oasen was tested both with pilot scale and batch experiment. The water of BW was tested only with a batch experiment. pCBA was used for the evaluation of the OH radical production. Thanks to its high reactivity with OH radical, pCBA enables this by measuring the variation of its concentrations.

Pilot scale experiments were performed at De Hooge Boom with water before and after DOC removal by ionic exchange. pH 7, 6.7 and 6.3 were tested with hydrogen peroxide concentrations of 2, 8 and 15 mg/l, with iron concentrations between 7 and 10 mg/l.

De Hooge Boom water was tested by batch experiment at pH 7 and 6, for contact times of 2 and 10 min and with a hydrogen peroxide concentration of 8 mg/l. The second batch experiment was conducted with the Waalwijk water. The tests were performed at pH 6.6, 6 and 3.5, for contact times of 2 and 10 min and with a hydrogen peroxide concentration of 2 and 8 mg/l.

The results proved that the water quality parameters influence the OH radical production. The used waters contained iron concentration between 7 and 10 mgFe total/l. These concentrations fit the Fenton process requirement, nevertheless different pCBA conversions were observed. The pilot scale experiments and the batch experiments using De Hooge Boom water type showed low conversion (<15%) of pCBA at high pH values. Even after decrease of NOM concentration, no significant pCBA conversion has been observed. The Fenton process did not work effectively, most likely because of formation of other than OH-radicals intermediates at higher pH values. Furthermore, alkalinity and different type and concentration of DOC could scavenge OH-radicals and thus reduce the fraction of OH-radical that is available for oxidation of micropollutants, in particular in De Hooge Boom water.

For Waalwijk batch experiment, depending on the experimental conditions the pCBA conversion increased from 18% (pH 6.6; [H_2O_2] = 2 mg/l; 2 min) to 99% (pH 3.5; [H_2O_2] = 8 mg/l; 10 min). The high pCBA conversion level indicates OH radical formation and low scavenging rate at low pH values.

The Fenton process can be efficient for water and wastewater treatment, but the process conditions as well as the water quality characteristics play a dominant role. Further investigations will be required to comprehend the role of the DOC fractions and the alkalinity on the hydroxide radical production.

Contents

1 Introduction

Dutch Water Supply companies produce drinking water that is safe to drink with respect to microbiological parameters (pathogens, biological stability) and chemical parameters. When considering the chemical water quality: sources may, however, contain organic micropollutants. In surface water treatment removal barriers such as activated carbon filtration, membrane filtration (nanofiltration, reverse osmosis) and oxidation processes (ozonation, UV-peroxide oxidation) are used. Groundwater generally does not contain organic micropollutants. Nevertheless, some sites have to cope with low concentrations of micropollutants. Apolar substances are generally well-removed by activated carbon. Polar substances, however, may be more problematic, because in the soil they prefer to stay in the water phase, and in the treatment these compounds are difficult to remove.

1.1 Aim of the study

In this report the investigation towards the applicability of the Fenton process is described. The Fenton process can be an effective way of treating water, to remove micropollutants without bromate formation and with respect to the costs. The Fenton process is an advanced oxidation process (AOP). Advanced oxidation processes use •OH, hydroxyl radicals to oxidize (in)organic compounds. This technology can be applied to the drinking water treatment practice. AOP includes several techniques such as O_3/H_2O_2, UV/H_2O_2, UV/O_3, UV and Fenton processes. Until now, UV/H_2O_2 is the only AOP applied at drinking water treatment in the Netherlands at one plant of Water supply company PWN.

1.2 The Fenton process

The principle of the Fenton process is the catalytic cycle of the reaction between iron (catalyst) and hydrogen peroxide (oxidant) to produce hydroxyl radicals (IJpelaar et al., 2000b). The hydroxyl radical is produced according to the following reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$$

The system has its maximum catalytic effect at pH 3. At higher pH, competition between the reduction of ferric to ferrous iron and the precipitation of ferric iron as hydroxide occurs and reduces the catalytic cycle efficiency (IJpelaar et al., 2001). Moreover, at pH values higher than 5, it is possible that the Fenton reaction produces another intermediate than the OH-radical, which is assumed to be the Ferry species. This intermediate is more selective than OH-radicals and therefore not equally efficient towards oxidation of different organic micropollutants and in general organic compounds (Hug and Leupin, 2003). Nevertheless, relevant organic pollutant degradation can be achieved by the ferrous iron concentration present in the groundwater and at ambient pH. At pH higher than 4 the single production of hydroxyl radicals may be sufficient to degrade the target compounds (IJpelaar et al., 2001). To enable an optimal production of radicals by reaction between Fe^{2+} and H_2O_2, the presence of oxygen should be prevented in order to prevent formation of iron(hydr)oxides, which take away the iron from the catalytic cycle. Thus, anaerobic water is required (IJpelaar et al., 2001).

1.3 Approach

Two types of groundwater are investigated, coming from the treatment plants 'De Hooge Boom' (Oasen) and Waalwijk (Brabant Water) in The Netherlands. Both pilot scale experiments and batch experiments were performed. To verify the performance of the Fenton process, the degradation of para-chloro benzoic acid (pCBA) was studied. pCBA reacts very fast with hydroxyl radicals and is expected to react slow with other possible intermediates such as Ferryl species (Elovitz and Von Gunten, 1999).

1.4 pCBA to evaluate OH radical formation

The direct measurement of the hydroxyl radicals in water is difficult because the steady-state concentration is low (Elovitz and Von Gunten, 1999). Rather than trying to directly measure the concentration of •OH during the Fenton process, a probe-compound which reacts with hydroxyl radicals can be used. The same probe-compound used by Elovitz and Von Gunten (1999) was used in this study and was para-chlorobenzoic acid (pCBA). pCBA has a very high reactivity with •OH ($k_{\bullet OH/pCBA} = 5 \times 10^9\ M^{-1}s^{-1}$). Because of this, the change in concentration of pCBA provides an indirect measurement of the hydroxyl radicals available for micropollutant oxidation. (Elovitz and Von Gunten, 1999). Thus, the use of pCBA enables the evaluation of the •OH production.

2 Experimental conditions

The Fenton process efficiency was investigated with two different types of anaerobic groundwater which came from two water treatment sites. The water types from Brabant Water (BW; Waalwijk) and Oasen (De Hooge Boom, Kamerik) were tested. The water of Oasen was tested both with pilot scale and batch experiment. The water of Brabant Water was tested only with a batch experiment.

2.1 Location

The pilot scale experiments were carried out at the water treatment plant 'De Hooge Boom' in Kamerik. It is operated by the Dutch drinking water supply company Oasen. At this plant anaerobic ground water is treated by rapid sand filtration and granular activated carbon. Batch experiments were carried out with water coming from 'De Hooge Boom' and from Waalwijk water treatment plant. The Waalwijk plant is operated by the Dutch drinking water supply company Brabant Water. At this plant anaerobic ground water is treated by aeration and rapid sand filtration.

2.2 Water compositions

Anaerobic groundwater was used for the experiments. The water compositions are shown in table 1. The analyses were performed at the laboratory of Kiwa Water Research in Nieuwegein.

Table 1: Composition of the investigated water types: 'De Hooge Boom' and 'Waalwijk'

Components	Results			Units
	De Hooge Boom (22/11/2007)	De Hooge Boom (13/12/2007)	Waalwijk (14/12/2007)	
Alkalinity (as HCO_3^-)	384	385	100	mg/l
Total iron*	6.7	10	8.3	
O_2	< 1	< 1	< 1	
DOC	7.1	2.7**	2.9	
Humic substances	4.53	0.98	na	
Building blocks	1.14	0.83	na	
Neutrals	0.77	0.55	na	

*: total iron was measured, the iron was assumed to be ferrous as a result of no oxygen content.
**: DOC was partly removed by the use of an anionic ion exchange.
na : not analysed

Table 2: Analysis specifications

Parameter	NPOC	Fe-total	H_2O_2	HCO_3^-	pCBA
Method	in accordance with ISO 8245 and NEN-EN 1484	in-house Kiwa method	in-house Kiwa method	in-house Kiwa method	in-house Kiwa method
Technique	NDIR	AAS-flame	Spectrophotometry	Titration	SPE on-line HPLC-UV
Detection limit	0.20 mg C/l in drinking water	0.10 mg Fe/l in drinking water	0.06 mg/l H_2O_2 in drinking water	6.1 mg HCO_3/l in drinking water	5 µg/l
Measurement uncertainty (Ue) %	6.4 (concentration level 4.0 mg/l)	not available	not available	3.6 (concentration level 100 mg HCO_3/l)	not available
Unit	mg C/l	mg/l Fe	mg H_2O_2 /l	mg HCO_3/l	µg/l
Apparatus	Shimadzu 5000A	Perkin Elmer AAS 3030 Paar Physica MX 350	Thermo Electron Unicam UV530	Metrohm Dosimat E535 Radiometer Nederland BV PHM 83	Perkin Elmer Binaryll pomp 250 Perlin Elmer LC 95 UV/Visible

2.3 Analytical techniques

The analytical methods used for DOC, Fe, H_2O_2, HCO_3^-, pCBA are given in table 2.
The analyses were performed at the laboratory of KWR in Nieuwegein.
All samples, except for the H_2O_2 analyses, were quenched with 1 g/l of sodium sulphite (Na_2SO_3) directly at the desired reaction time. The addition of sulphite quenches the reaction between iron and peroxide by a rapid reaction with peroxide which is then not available for radical production anymore.

2.4 Materials and chemicals

Table 3: list of materials and chemicals

Compound	**Quality**	**Supplier**
Hypochloric acid, 30%	Technical grade	Chemproha
Hydrogen peroxide, 35%	-	Chemproha
4 chlorobenzoic acid 99% (pCBA)	Analytical grade	JT Baker, casnr. 7757-83-7
Sodium sulphite (Na_2SO_3)	Analytical grade	SAF Sigma, casnr. 74-11-3
Ion exchange resin Lewatit VP OC 1071	-	Caldic

2.5 De Hooge Boom

2.5.1 Pilot scale experiment

The experiments were performed at De Hooge Boom. In figure 1 the set up of the pilot plant is given. The feed flow of the anaerobic raw water was remained constant at 5 m³/h. The hydrogen peroxide concentration of the stock solution was measured each day at the start of the experiments to determine the dosing of the pump.

Before the start of the experiment the raw water was sampled for iron, DOC, and HCO_3^- analysis. Then hydrogen peroxide was dosed to the feed flow. After 15 minutes a sample was taken for hydrogen peroxide measurement. Afterwards, the hydrogen peroxide addition was stopped and the pCBA was dosed to the feed flow for 15 minutes. pCBA samples were taken for the analysis to measure the influent concentration.

The experiments were performed according to the different conditions described in table 4 and 5. With a dosing pump, hydrochloric acid was added to adjust the pH and the pCBA was dosed to a concentration of 400 µg/l. The water was directed through a first static mixer to blend the solution. After this static mixer, the hydrogen peroxide was added, passing a second static mixer. After 15 minutes of stabilisation time under experimental conditions, samples were taken for pCBA and hydrogen peroxide analysis. The total contact time for the Fenton reaction to take place was 2 minutes. Directly after sampling the pCBA samples were quenched with 1 g Na_2SO_3/l.

The experiments of 22nd November 2007 and 13th December 2007 were performed according to the procedure which is described above. However, during the experiment of 13th December 2007, the raw water was treated by ionic exchange for a partial removal of DOC (7.1 to 2.7 mgC/l, see Table 1).

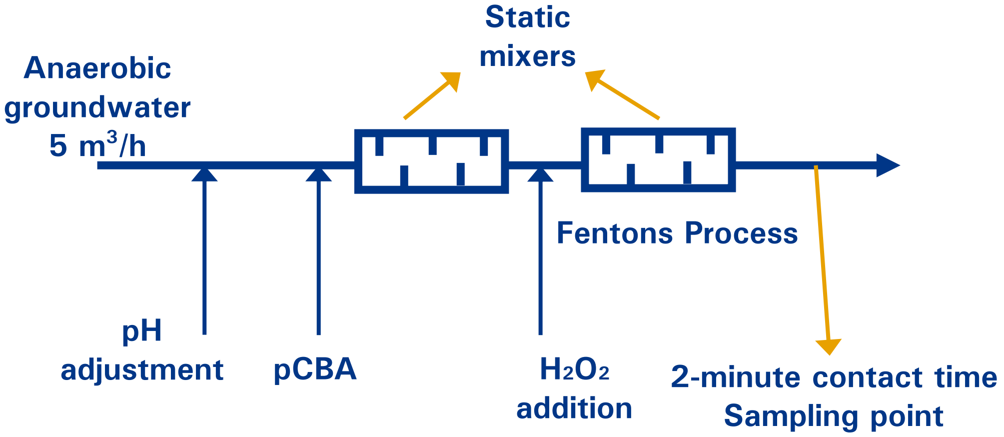

Figure 1: scheme of the pilot plant at location "De Hooge Boom" in Kamerik (Oasen)

Table 4: experimental conditions, experiment of 22nd November 2007, De Hooge Boom

pH	pCBA (µg/l)	H_2O_2 (mg/l)	contact time (min)
7	400	-	2
7	400	8	2
7	400	15	2
6.5	400	8	2
6.5	400	15	2
6	400	8	2
6	400	15	2

Table 5: experimental conditions, experiment of 13th December 2007, raw water after DOC removal

pH	pCBA (µg/l)	H_2O_2 (mg/l)	contact time (min)
7	400	2	2
7	400	8	2
7	400	15	2
6.5	400	2	2
6.5	400	8	2
6.5	400	15	2
6	400	2	2
6	400	8	2
6	400	15	2

2.5.2 Batch experiment

Batch experiments were performed with the anaerobic waters from De Hooge Boom.
Green glass bottles at 1l were used to avoid reaction with light. The bottles were filled with raw water. Instantaneously, the pH was adjusted and pCBA was added according to table 6. Then hydrogen peroxide was added. The bottles were closed and the samples were stirred. The Fenton process was stopped after 2 and 10 minutes by quenching with 1 g Na_2SO_3/l.

Table 6: anaerobic raw water ps. 'De Hooge Boom', experimental conditions, experiments of 27th September 2007

pH	pCBA (µg/l)	H_2O_2 (mg/l)	Contact time (min)
7	400	-	-
7	400	8	2
7	400	8	10
6	400	8	2
6	400	8	10

2.6 Waalwijk

2.6.1 Batch experiment

Batch experiments were performed with the anaerobic waters from 'Waalwijk'.
Green glass bottles at 1l were used to avoid reaction with light. The bottles were filled with raw water. Instantaneously, the pH was adjusted and pCBA was added according to table 7. Then hydrogen peroxide was added. The bottles were closed and the samples were stirred. The Fenton process was stopped after 2 and 10 minutes by quenching with 1 g Na_2SO_3/l.

Table 7: anaerobic raw water ps. 'Waalwijk water', experimental conditions, experiments of 14th December 2007

pH	pCBA (µg/l)	H_2O_2 (mg/l)	Contact time (min)
6.6	400	-	-
6.6	400	8	2
6.6	400	8	10
6.6	400	2	2
6.6	400	2	10
6	400	8	2
6	400	8	10
6	400	2	2
6	400	2	10
3.5	400	8	2
3.5	400	8	10
3.5	400	2	2
3.5	400	2	10

3 Results and discussions

3.1 De Hooge Boom experiments

3.1.1 Pilot scale

The results of the experiments of the 22nd of November 2007 are shown in figure 2. The pCBA oxidation by the Fenton process was investigated using a pilot with water of De Hooge Boom.

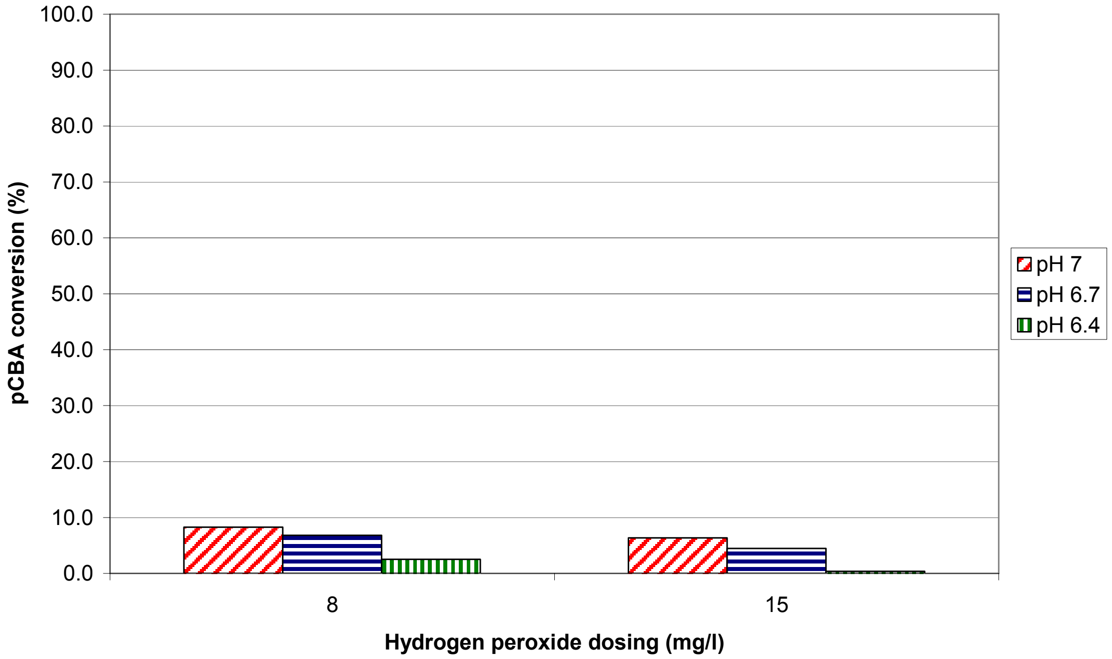

Figure 2: pCBA conversion from anaerobic raw water ps. 'De Hooge Boom' by Fenton oxidation process at three different pH, experiment of 22nd November 2007

Due to problems with the dosing system the lowest pH of the experiment was 6.36 after hydrochloric acid addition, whereas pH 6.0 was desired. The hydroxide peroxide concentration of the stock solution was measured daily and the dosage flow was adjusted to gain the right hydrogen peroxide concentration.
The efficiency of the Fenton process can be observed on pCBA conversion (see figure 2). Taking into account the accuracy of the experiments and analysis, no pCBA can be considered as oxidised. The OH radical production is supposed to be low.
The hypothesis which could explain this low conversion was that the high DOC concentration affected the oxidation process and so it restricted the pCBA oxidation. For that reason also an experiment was performed after removal of DOC by anion exchange. The figure 3 shows the results of this second experiment.
During the second experiment at 'De Hooge Boom', the DOC concentration decreased from 7.1 to 2.7 mg C/l. The removals of the DOC fractions were 78%, 27% and 29% for respectively humic substances, building blocks and neutrals. In this experiment, the initial pCBA concentration was 400 µg/l and three hydrogen peroxide concentrations were tested 2, 8 and 15 mg/l. The different pH values of the experiment are similar as the pH values used during the previous experiment. Comparing the results with and without the removal of DOC by ion

exchange, there is no clear improvement of the conversion of pCBA. The pCBA conversion is still low (<12%) even though the DOC concentration was decreased 2.5 times.

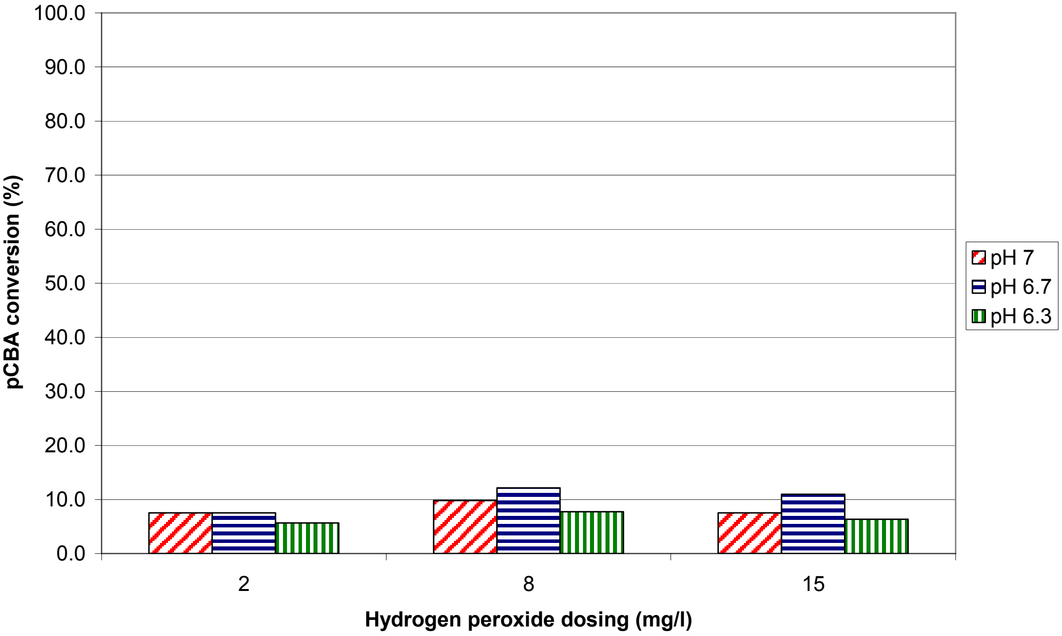

Figure 3: pCBA conversion from anaerobic raw water after treatment with IEX ps. 'De Hooge Boom' by Fenton oxidation process at three different pH, experiment of 13th December 2007

3.1.2 Batch experiment

Batch experiments were performed using 1l bottles and raw water from the De Hooge Boom water treatment plant. Several experimental conditions were investigated. Table 8 shows the results. The experiments were carried out with 8 mg/l of hydrogen peroxide, both pH 7 and 6, and reaction times of 2 and 10 minutes.

Both reaction times (2 and 10 minutes) seem to have a similar effect on the pCBA conversion. In both cases the pCBA conversion is 15% average. In addition, the decrease of the pH from 7 to 6 did not affect the oxidation efficiency. The absence of difference between 2 and 10 min shows that an interference reaction seems to proceed within 2 min. The pCBA conversion values are low, this means that the OH radical production seems to be low with this water type. The obtained results are in accordance with the results of the pilot scale experiments. This confirms that the conditions during the pilot tests at De Hooge Boom were correct.

Table 8: pCBA conversion from anaerobic raw water ps. 'De Hooge Boom' by Fenton oxidation process, experiment of 26th September 2007.

pH	H_2O_2 dosing (mg/l)	Contact time (min)	pCBA concentration (µg/l)	pCBA conversion (%)
7.04	0	-	384	-
7.04	8	2	331	14
7.04	8	10	329	14
6.00	8	2	326	15
6.00	8	10	321	16

3.1.3 Discussion

According to the theory of the Fenton process (IJpelaar et al., 2000a), the experiments were performed under pH, hydrogen peroxide concentration and iron concentration which were able to promote the oxidation. However, the results of the two pilot scale experiments show that the Fenton oxidation process does not work efficiently with the water of the 'De Hooge Boom' and so no relevant pCBA conversion was observed.

The pCBA conversion was used to quantify the hydroxyl radical formation but with the obtained results the hydroxyl radical formation cannot be confirmed. Thus the absence of pCBA oxidation could be explained by: 1) no or low radical formation or 2) interference oxidation reactions with other compounds (organic or inorganic compounds) during the experiments. In addition, no better pCBA oxidation was measured when DOC partially was removed. Either the DOC concentration did not affect the oxidation process or the specific DOC fractions partially removed (humic substances, building blocks and neutrals) by ionic exchange were not responsible for the oxidation interferences. Finally, high alkalinity (HCO_3^-) is known to be an effective scavenger of hydroxyl radicals. Concentration of 380 mg/l is high and could have an effect on the limitation of the oxidation reaction. According to the AquaCalc 3.1 calculation, the decreases of the pH to 6.3 and 6 decreased the bicarbonate concentration to 197 and 127 mg/l respectively. However these decreases of the bicarbonate concentration were not sufficient to improve the pCBA conversion. Weeks and Rabani (1966) show that bicarbonate ions (HCO_3^-) and carbonate ion (CO_3^{2-}) are known scavengers of •OH.

According to the results of De Hooge Boom experiment, the water quality which is used for Fenton process seems to affect the efficiency of the oxidation reaction. However the limitation factor was not identified and further investigations would be useful.

3.2 Waalwijk batch experiments

Experiments at a laboratory scale were performed using 1l bottles and anaerobic raw water from the 'Waalwijk' water treatment plant. Several experimental conditions were investigated. The results are shown in figure 4 and 5.

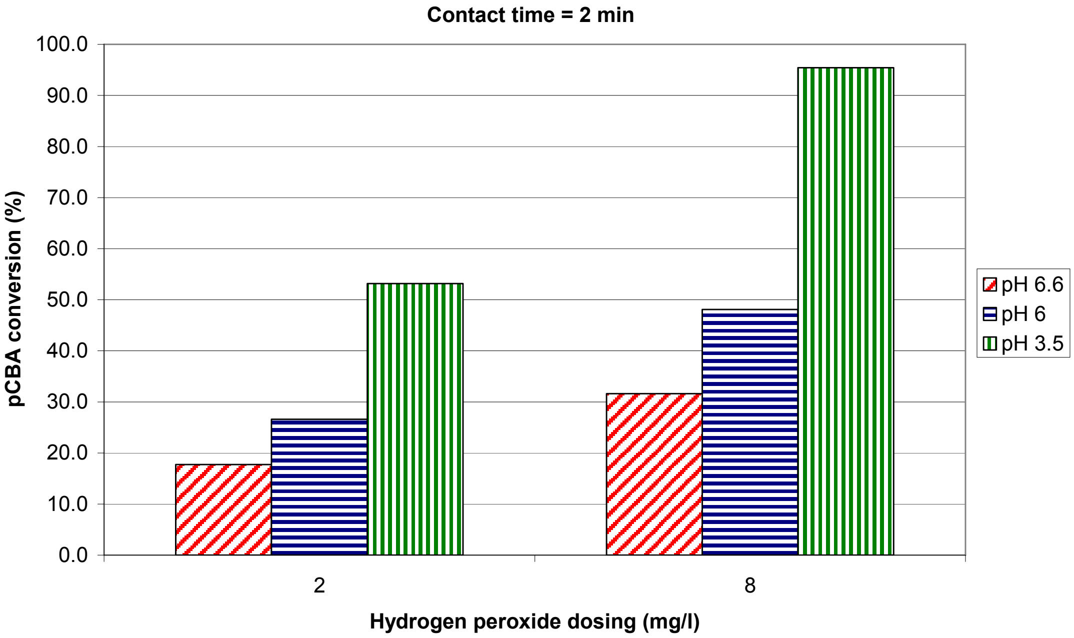

Figure 4: pCBA conversion from anaerobic raw water from 'Waalwijk' by Fenton oxidation process, contact time 2 min, experiment of 14th December 2007

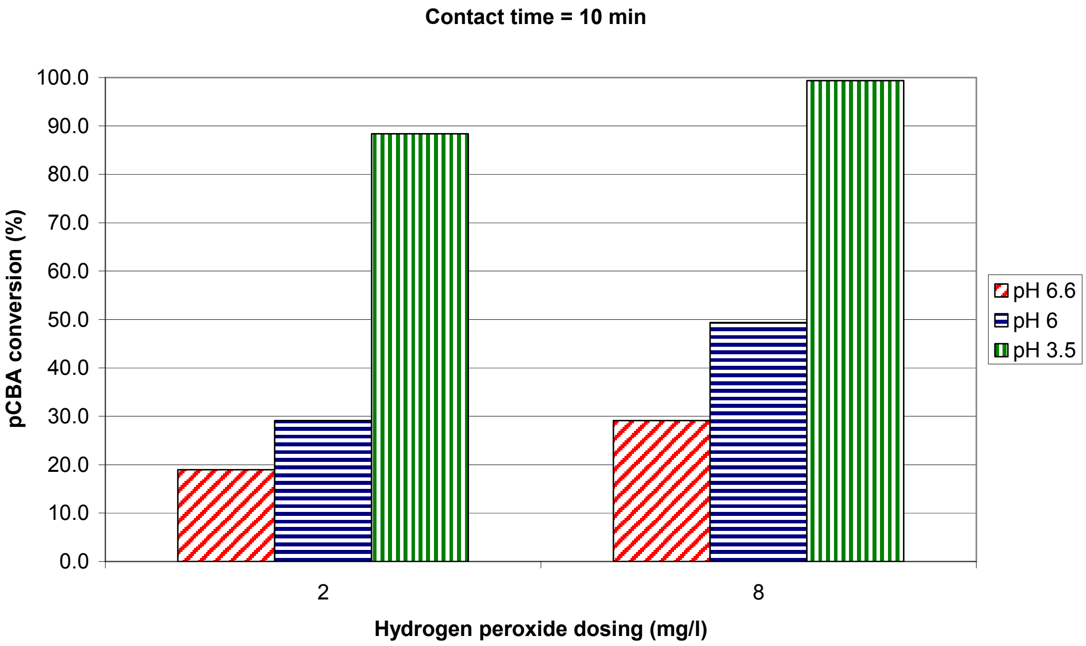

Figure 5: pCBA conversion from anaerobic raw water from 'Waalwijk' by Fenton oxidation process, contact time 10 min, experiment of 14th December 2007

Both pH and hydrogen peroxide concentration have an effect on the pCBA conversion. For the three investigated pHs, the pCBA conversions were higher with 8 mg/l than with 2 mg/l of hydrogen peroxide. The decrease of the pH enhanced the pCBA conversion. At both pH 6.6 and 6, the contact time did not modify the pCBA conversion, however at pH 3.5 the reaction time affected the conversion efficiency of pCBA. The most efficient conversion occurred after 10 minute of reaction time. This depends on the experimental conditions. The pCBA conversion increased from 18 % (pH 6.6; $[H_2O_2]$ = 2 mg/l; 2 min) to 99 % (pH 3.5; $[H_2O_2]$ = 8 mg/l; 10 min). In this experiment a relevant pCBA conversion has been observed. In water treatment plant, it is not workable to lower the pH to 3.5, it might be better to increase the peroxide concentration at pH 6 and see if that has an effect on the hydroxyl radical formation thanks to the Fenton process.

3.3 Comparison of results of De Hooge Boom and Waalwijk

Under similar conditions (pH 6 and 8 mg/l of hydrogen peroxide), 49 % and 16 % of pCBA were removed for respectively Waalwijk and De Hooge Boom. The alkalinity is 3.8 times higher for the De Hooge Boom water and DOC concentration of both waters were different and could explain the difference of oxidation efficiency. Table 9 shows the scavenging rate of the different water types. It is assumed that only bicarbonate ions and DOC scavenge the OH radicals, according to the following formula (pers. comm. Katsoyiannis, 2008):

$$scavenging\ rate = k_{OH,DOC}\left[DOC\right] + k_{OH,HCO3-}\left[HCO_3^-\right]$$

In which

$k_{OH,DOC}$ reaction rate constant between organic matter and OH radicals = 2.5 x 10^4 l mg^{-1} s^{-1} (pers. comm. Katsoyiannis, 2008)

$\left[DOC\right]$ organic matter concentration in mg/l

$k_{OH,HCO3-}$ reaction rate constant between bicarbonate ions and OH radicals = 8.5 x 10^6 M^{-1} s^{-1} (pers. comm. Katsoyiannis, 2008)

$[HCO_3^-]$ bicarbonate concentration in mol/l

Then the pCBA conversion rate (by OH radicals) can be compared to the scavenging rate (table 9). The scavenging caused by pCBA is calculated by multiplying the reaction rate constant of pCBA and OH radicals (5x10^9 M^{-1} s^{-1} (Elovitz and Von Gunten, 1999)) by the pCBA concentration in mol/l (using a molar mass of 156.6 g/l).

The data in Table 9 show for all experiments a higher scavenging rate than the pCBA conversion rate. This is mainly due to the high DOC scavenging rate. The rate constant for DOC is however the least well-known, as DOC is a mixture of several types of organic molecules. And the composition is different for every water type.
So the calculations do not really help in establishing why the pCBA conversion in the water from Waalwijk is much better than that in the water from Kamerik. So it might be concluded that the concerned primary water quality parameters that influence the OH radical production are not clearly identified yet.

Table 9: pCBA conversion rate compared to the scavenging rate in the different waters tested. (r = rate)

Water type	pH	[DOC] (mg/l)	$[HCO_3^-]$ (mg/l)	r_{DOC}	r_{HCO3-}	r_{scav}	r_{pCBA}
Kamerik	7	7.1	385	1.78E5	5.36E4	2.31E5	1.05E4
Kamerik	6	7.1	127	1.78E5	1.77E4	1.95E5	1.05E4
Kamerik (after IEX)	7	2.7	385	6.75E4	5.36E4	1.21E5	1.28E4
Kamerik (after IEX)	6.3	2.7	197	6.75E4	2.75E4	9.50E4	1.28E4
Waalwijk	6.6	2.9	100	7.25E4	1.39E4	8.64E4	1.28E4
Waalwijk	6	2.9	42	7.25E4	5.85E3	7.84E4	1.28E4
Waalwijk	3.5	2.9	0.2	7.25E4	2.79E1	7.25E4	1.28E4

4 Conclusions

The efficiency of the Fenton process has been investigated with two types of water, 'De Hooge Boom' and 'Waalwijk'. With the conversion of pCBA, the production of OH radicals in both water types is investigated. Both types of water seemed to have the right characteristics to successfully favour the Fenton process reaction and to observe pCBA conversion. Anaerobic waters were used containing iron (Fe^{2+}) (8-10 mg/l Fe total) to react with H_2O_2 to form hydroxyl radicals.
Pilot scale experiments with 'De Hooge Boom' water and batch experiments with 'De Hooge Boom' and 'Waalwijk' waters were performed.

With the De Hooge Boom water, the pilot scale experiments and the batch experiments showed that the Fenton process did not work effectively. No relevant conversion (<15%) of pCBA was observed. Even after decrease of NOM concentration, no pCBA conversion has been observed which indicate that the fractions of DOC which scavenge the hydroxyl radicals were probably not removed after treatment with ion exchange. In general, the understanding of the reactions and interference reactions which happened in the water during the experiments is not achievable. The results of the pilot scale test have been confirmed by the batch experiment for the water of 'De Hooge Boom'. For the water of 'De Hooge Boom', low pCBA conversion was found.

For the water of 'Waalwijk' a relevant rate of pCBA conversion was observed during the batch experiment. This result could be explained by the different DOC composition and the difference of alkalinity between the both water types. However no reliable explanation has been found to support the difference of oxidation efficiency so far. Nevertheless, it underlines that the water quality and the water composition can strongly affect the formation and the reaction of the hydroxyl radicals and so the oxidation of compounds of interest.

The Fenton process can work; even at ambient pH, but the water matrix and mainly the concentration of alkalinity, the type and concentration of DOC and the presence of different ligands play a prominent role in the formation and scavenging of oxidizing intermediates, which in turn determine the efficiency of the method towards micropollutant oxidation.

5 Recommendations

Further investigations on the water quality effects on the Fenton process efficiency should be carried out, particularly for De Hooge Boom water, to explain the low pCBA conversion.

To investigate the alkalinity role on the Fenton process efficiency, experiments under different alkalinity levels should be performed. The alkalinity of the De Hooge Boom water can be reduced and the alkalinity of the Waalwijk water can be increased. Thus, comparison between the Fenton process efficiencies of both waters at similar alkalinity will be feasible.

The effects of the DOC on the Fenton process should be investigated. Different concentrations and compositions of DOC can be tested for the effect on OH radical formation.

Prior to perform experiments to pilot or large scale, batch experiments can be carried out as a simple method to control the performance of the Fenton process.

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