Combination of Fenton oxidation process and ceramic nanofiltration

Efficiency during groundwater treatment in Waalwijk plant
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Acknowledgements
The authors wish to thank Brabant Water for the permission to perform the experiment at the Waalwijk water treatment plant. We are grateful to Toon Schellekens and Stephan van de Wetering for support and help during the experiments.

This report is: PU = public
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1 Introduction

1.1 Background

About 2/3 of the Dutch Drinking water is produced from groundwater sources. The majority of these sources are anaerobic and contain moderate to high levels of ferrous (Fe(II)) iron and manganese. Furthermore, the water is acidic due to high carbon dioxide contents. In many cases the water contains also ammonium, methane and hydrogen sulphide. Treatment of these sources is done by conventional aeration and filtration systems. Depending on the solute levels, a single or double aeration-filtration step is required. About 50 % of the treatment plants also utilize pellet softeners for hardness reduction and conditioning.

Recent investigations have indicated that organic micropollutants may be present in ground water sources as well.

The acidic and anaerobic conditions, and the presence of ferrous iron are favourable for application of Fenton’s reaction. The addition of hydrogen peroxide to the water will initiate this reaction in which hydroxyl radical are formed. These radicals will oxidise organic compounds present in the water very rapidly and will destroy micropollutants.

The idea tested in this research is the application of ceramic nanofiltration (CNF) membranes after the Fenton reaction. With the Fenton reaction, the organic micropollutants will be destroyed, while the CNF will remove the reaction products (AOC, metabolites, and Ferric hydroxides) and other water constituents such as hardness, remaining ferrous iron, manganese etc. After the CNF an aeration and filtration step is still required to remove dissolved gases and to remove ammonium by biofiltration, but it is expected that this filter step can have a much smaller footprint. The combined Fenton CNF process may therefore form an interesting alternative ground water treatment system.

1.2 Aim of the project

In this experiment the combined process of Fenton reaction (Fe$^{2+}$+H$_2$O$_2$) and ceramic nanofiltration will be tested as a new innovative ground water treatment. Hydrogen peroxide will be added to anaerobic groundwater at WTP Waalwijk of Brabant Water. Before addition, acid is dosed for pH control. The following research questions will be answered:

- What is the effectiveness of the Fenton reaction? What is the amount of hydroxyl radicals formed?
- Are organic contaminants removed by the Fenton and ceramic NF?
- What is the AOC production by Fenton and can it be removed by C-NF?
- What is the remaining Fe and Mn content after C-NF?
- What is the removal of ions and salts by C-NF?
1.3 Approach

To test the idea for the new ground water treatment scheme, a small pilot plant with ceramic NF membranes was rented. The plant was placed at the Waalwijk pumping station of the water supply company “Brabant Water”. In a previous study, it was found that the Fenton reaction was very effective in this water. The CNF pilot plant was connected to the raw water mains at the pumping station. The idea was to have a continuously running system, where hydrogen peroxide was added to the feed water prior to the membranes. Also micropollutant spiking experiments were planned, with analyses of the membrane feed, permeate and concentrate to see the effectiveness of removal. Hydroxyl radical formation would be tested by pCBA (p-chloro benzoic acid). Also the formation of biodegradable compounds would be tested by AOC analysis and removal of inorganic compounds by the membrane were to be investigated by sampling and analysis.

1.4 Theoretical part

1.4.1 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 [2]. The hydroxyl radical is produced according to the following reaction:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \bullet \text{OH} \]

The system has its maximum catalytic effect at a pH of 3. At higher pH, competition between reduction of ferric to ferrous iron and the precipitation of ferric iron as hydroxide occurs and reduces the catalytic cycle efficiency [3]. Nevertheless, relevant organic pollutant degradation can be achieved by the ferrous iron concentration present in the groundwater and at ambient pH. Thus at pH higher than 4 the single production of hydroxyl radicals may be sufficient to degrade the target compounds [3]. To enable an optimal production of radicals by reaction between Fe$^{2+}$ and H$_2$O$_2$, the presence of oxygen should be prevented, anaerobic water is required [3].

1.4.2 Role of pCBA

The direct measurement of the hydroxyl radicals is difficult on water solution because the steady-state concentration is low [1]. Rather than trying to directly measure the concentration of $\bullet$OH during the Fenton process, a probe-compound which reacts with hydroxyl radicals was used. As [1], the probe-compound used in this study was para-chlorobenzoic acid (pCBA) because it has a very high reactivity with $\bullet$OH ($k_{\text{OH/pCBA}} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) [1]. The change in concentration of pCBA provided an indirect measurement of the $\bullet$OH concentration [1]. The use of pCBA enabled the evaluation of the $\bullet$OH production.
2 Experimental conditions

2.1 Location

The experiments were carried out at WTP Waalwijk. It is a pumping station operated by the Dutch drinking water supply company Brabant Water. At the plant anaerobic ground water was treated by aeration and rapid sand filtration. The location was selected because good results were achieved with Fenton’s reaction at this site (see Techneau report: “Fenton process for Contaminant Control”).

2.2 Water composition

Anaerobic groundwater was used for the experiments. The water was abstracted from the feed mains to one of the filters at the treatment plant. The water composition of the used raw water is shown in the table 1, the values are the averages of the analysis which were performed during the year 2006 by Brabant Water and the analytical results which were measured the 7th March 2008.

<table>
<thead>
<tr>
<th>Components</th>
<th>Analysis KWR 07/03/2008</th>
<th>Average values¹ 01/01/2006-21/12/2006</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>34</td>
<td></td>
<td>mg/l</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>117</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>29.3</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>52.3</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>12</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>33</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>&lt; 4.5</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>8.0</td>
<td>8.25</td>
<td></td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.353</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>&lt;0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>11.4</td>
<td></td>
<td>°C</td>
</tr>
<tr>
<td>pH</td>
<td>6.8</td>
<td>6.71</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>28.0</td>
<td>33</td>
<td>mS/m</td>
</tr>
</tbody>
</table>

¹ Results from Brabantwater
2.3 Pilot used

A pilot plant was rented from Inopor\(^2\) for these experiments. It consisted of one 53l tank, one pump to establish the required feed pressure and cross-flow velocity and three membrane modules. Permeate, concentrate and recirculation flows were monitored by rotameters. The nanofiltration experiments were carried out at a recovery of approximately 50%. All test unit parts in contact with the solution were made of stainless steel to avoid absorption of materials in test unit. A picture of the pilot is shown in appendix 5.1 and the figure 1 presents a flow diagram. A detailed flow diagram of the pilot is shown in appendix 5.2.

The membrane used was a TiO\(_2\) ceramic membrane which was able to resist to experimental oxidant condition. Its molecular weight cut off was 450D, its mean pore size was 0.9 nm and its clean water permeability was 20 l.m\(^{-2}\).h\(^{-1}\).bar\(^{-1}\). Three block modules were used. Each block contained 19 channels of 3.5 mm diameter and an outer diameter of 25mm. One module was 1.20 m length having a membrane area of 0.25 m\(^2\) and the two other modules were 0.50 m with a membrane area of 0.10 m\(^2\). The total membrane area was 0.45 m\(^2\).

![Flow diagram of the used pilot](image)

**Figure 1: flow diagram of the used pilot**

2.4 Analysis

During these experiments, several parameters were analysed. Samples of feed, concentrate and permeate were collected to measure the concentrations of ions: Fe\(^{2+}\), Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4^{2-}\) and HCO\(_3^-\). This sampling was performed once to measure the membrane retention. The Kiwa Water Research laboratory performed the analysis.

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\(^2\) Inopor GmbH, Michael-Faraday-Str. 1, D-07629 Hermsdorf, Germany; https://www.inopor.com
pCBA (p-chloro benzoic acid) has been used to evaluate the Fenton process reaction, thus for each experiment the feed, concentrate and permeate were sampled and analysed. The KWR laboratory performed the analysis. The AOC concentration was analysed in feed, concentrate and permeate during two experiments. HWL carried out the analysis. During the experiments, pH, conductivity and O₂ concentration were measured in feed and recirculation loop. The hydrogen peroxide was titrated using permanganate and sulfuric acid before experiments.

2.5 List of Chemicals

Different chemicals have been used for the experiments and for the cleaning of the membrane.

- For the experiments:
  - Hydrochloric acid (37%-38%), for pH adjustment
  - Hydrogen peroxide (0.86g/l), dilution of hydrogen peroxide 30% solution with MilliQ water.
  - pCBA (40mg/l), analyse quality powder dissolved in MilliQ water.
  - Sodium sulphite, to stop oxidation reaction in sample bottles

- For cleaning:
  - Alkaline cleaning agent (1%) provided by pilot supplier
  - Acid cleaning agent (1%) provided by pilot supplier
  - Oxalic acid (1%)

2.6 Experimental procedure

The experiments were carried out in batch mode. The pilot was entirely emptied. Then, using nitrogen, the air was removed from the pilot tubes and tank. The concentration of oxygen was measured with the oxygen sensor on several points and it had to be lower than 0.05 mg/l of oxygen. To keep the system anaerobic, nitrogen bubbling occurred in the tank. The tank was filled with raw water. Then the pilot tubes were filled by paying attention no air comes in. The volume of water in the system was estimated at 50l. Hydrochloric acid was added to adjust the pH which was measured in the tank using pH-meter.

pCBA (500 ml) was added in the tank. A sample of the homogeneous solution was picked up to know the exact pCBA concentration.

Depends on the experimental conditions, 350ml or 115ml of hydrogen peroxide was added and the pilot was switched on. The feed pressure was adjusted to 18 bars. The permeate flows, concentrate flows, the feed pressures and the pressures after each module were written down. The pH, the conductivity and the oxygen concentration were measured in tank during the runs. After 6 minutes, permeate and bleed were sampled for pCBA analysis.
Sodium sulphite was added in all samples to stop the oxidation reaction and obtain a concentration of 0.3g/l. The pilot was stopped and emptied. If the permeate flow was higher than 40l/h at 18 bars feed pressure, the next experiment was carried out, otherwise the cleaning of the membrane was required and performed.

The first experiment using hydrogen peroxide and pCBA was stopped after 30 minutes instead of 6 minutes, and several samples were picked up.

The membrane retention experiment, was performed in feed and bleed mode with a feed pressure of 12 bars. The sampling was done after 25 min.

2.7 Cleaning procedure

Different cleaning procedures have been tested.
- Pilot supplier procedure, the membrane was cleaned with alkaline solution during 30 min. The pilot was rinsed and then 30 min of acid cleaning were performed. The pilot was rinsed. Tap water was used. This procedure was not effective to recover the right permeate flow.
- Oxalic acid, a solution of 1% oxalic acid in tap water was used. This procedure worked but during the rinse with tap water, a permeate flow decreasing was observed.
- Oxalic acid with MilliQ water, it was effective and the used procedure is described above.

After an experiment, the pilot was entirely emptied. The pilot was filled with 20 liter of MilliQ water containing 1% of oxalic acid. The cleaning program was started. Thus the cleaning solution recirculated during 30 min without pressure in the pilot. The temperature of the solution increased from 20°C to approximately 50°C. The pH of the cleaning solution was between 0.9 and 1.3. At the end of the cleaning, the pressure was applied on the feed flow, 18 bars and the permeate production was measured. If the permeate flow was still lower than 40 l/h at 18 bars, a second cleaning run was performed. After the circulation of the cleaning solution, the pilot was entirely emptied and rinsed with MilliQ water.
At the end of the daily experiment, the cleaning solution was let in the pilot for a night soaking of the membrane.

2.8 Experimental conditions

Four different oxidative conditions have been investigated: 1) pH 4 and [H₂O₂] = 6mg/l ; 2) pH 4 and [H₂O₂] = 2mg/l ; 3) pH 6 and [H₂O₂] = 6mg/l and 4) pH 6 and [H₂O₂] = 2mg/l.

First, the blank experiment was carried out using no chemical, just ceramic nanofiltration membrane. The feed pressure was 12 bars.
Second, pCBA blank experiments were performed at pH 4 and pH 6. The experiments were performed according to the procedure described in section 2.6; only the hydrogen peroxide was not added.

Third, the oxidation experiments were performed according to the procedure described in section 2.6 and for the four different conditions (See table 2).

**Table 2: Overview of experiments and conditions**

<table>
<thead>
<tr>
<th>Date</th>
<th>experiments</th>
<th>pH</th>
<th>[H₂O₂]</th>
<th>pCBA</th>
<th>Sampling</th>
<th>Cleaning agent</th>
<th>Rinse solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>07/03</td>
<td>cleaning</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – tap water</td>
<td>Tap water</td>
</tr>
<tr>
<td></td>
<td>Blank 1</td>
<td>6.8</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Ion analysis</td>
<td>/             /</td>
</tr>
<tr>
<td>13/03</td>
<td>cleaning</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – MilliQ water</td>
<td>MilliQ water</td>
</tr>
<tr>
<td></td>
<td>Exp 1</td>
<td>4</td>
<td>6mg/l</td>
<td>400µg/l</td>
<td>pCBA</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>Cleaning and soaking</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – MilliQ water</td>
<td>MilliQ water</td>
</tr>
<tr>
<td>14/03</td>
<td>Blank 2</td>
<td>4</td>
<td>0mg/l</td>
<td>400µg/l</td>
<td>pCBA</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>Blank 3</td>
<td>6</td>
<td>0mg/l</td>
<td>400µg/l</td>
<td>pCBA</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>cleaning</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – MilliQ water</td>
<td>MilliQ water</td>
</tr>
<tr>
<td></td>
<td>Exp 2</td>
<td>4</td>
<td>6mg/l</td>
<td>0µg/l</td>
<td>AOC</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>Cleaning and soaking</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – MilliQ water</td>
<td>MilliQ water</td>
</tr>
<tr>
<td>17/03</td>
<td>Exp 3</td>
<td>6</td>
<td>2mg/l</td>
<td>400µg/l</td>
<td>pCBA</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>cleaning</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – MilliQ water</td>
<td>MilliQ water</td>
</tr>
<tr>
<td></td>
<td>Exp 4</td>
<td>4</td>
<td>2mg/l</td>
<td>400µg/l</td>
<td>pCBA</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>Exp 5</td>
<td>6</td>
<td>6mg/l</td>
<td>400µg/l</td>
<td>pCBA</td>
<td>/</td>
<td>/             /</td>
</tr>
<tr>
<td></td>
<td>cleaning</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Oxalic acid – MilliQ water</td>
<td>MilliQ water</td>
</tr>
<tr>
<td></td>
<td>Exp 6</td>
<td>4</td>
<td>6mg/l</td>
<td>400µg/l</td>
<td>pCBA and AOC</td>
<td>/</td>
<td>/             /</td>
</tr>
</tbody>
</table>
3 Results and discussions

3.1 pCBA oxidation

The efficiency of the Fenton oxidative process has been investigated using para-chlorobenzoic acid. The table 3 shows the results of the oxidation coupled with the ceramic nanofiltration. The experiments were carried out under pH 4 and 6 and with hydrogen peroxide concentrations of 2 mg/l and 6 mg/l. The samplings were done after 6 minutes of experiments. The percentage removal is calculated between the initial feed concentration and the permeate concentration. The removal by nanofiltration of pCBA is not expected because the pCBA molecular weight is 157 g/mol which is lower than the molecular weight cut-off of the membrane.

Table 3: pCBA concentration and removal at different experimental conditions, Fenton process oxidation and ceramic nanofiltration.

<table>
<thead>
<tr>
<th>pH</th>
<th>H₂O₂ (mg/l)</th>
<th>H₂O₂ corrected value (mg/l)</th>
<th>Feed t=0 min (µg/l)</th>
<th>Concentrate t=6min (µg/l)</th>
<th>Permeate t=6min (µg/l)</th>
<th>pCBA conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Blank</td>
<td>0</td>
<td>325</td>
<td>330</td>
<td>325</td>
<td>0</td>
</tr>
<tr>
<td>pH 4</td>
<td>6</td>
<td>5,3</td>
<td>350</td>
<td>&lt;5</td>
<td>7</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1,2</td>
<td>240</td>
<td>44</td>
<td>46</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Blank</td>
<td>0</td>
<td>355</td>
<td>370</td>
<td>350</td>
<td>1</td>
</tr>
<tr>
<td>pH 6</td>
<td>6</td>
<td>5,0</td>
<td>335</td>
<td>81</td>
<td>85</td>
<td>75</td>
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<tr>
<td></td>
<td>2</td>
<td>1,7</td>
<td>345</td>
<td>155</td>
<td>155</td>
<td>55</td>
</tr>
</tbody>
</table>

According to the blank experiment results, without hydrogen peroxide no pCBA was removed from the solution. The pCBA destruction did not occur in these experimental conditions. The concentrations of pCBA were similar in feed, concentrate and permeate, so no pCBA retention was observed during filtration. This result was expected because the molecular weight of the pCBA is 157 g/mol 2.5 times lower than the molecular weight cut-off of the membrane which was 400. Fenton process works better at low pH and high hydrogen peroxide concentration. At the most effective condition, pH 4 and 6 mg/l of hydrogen peroxide, 98 % of pCBA removal was observed. The efficiency of the process decreases when the pH is increased and the hydrogen peroxide concentration decreased. At the less effective condition, pH 6 and 2 mg/l of hydrogen peroxide still 55 % of pCBA removal was observed. The bottle experiments
performed at pH 6 and 2 mg/l of hydrogen peroxide presented a pCBA conversion of 28% average (see Techneau report: “Fenton process for Contaminant Control”). This value is lower than the result in table 3, maybe due to difficulty to keep bottle system anaerobic.

In the table 4, the rate of the pCBA removal reaction is presented. After 3 minute the reaction was not achieved, 11 µg/l of pCBA were measured. However after 10 minute, the pCBA concentration was below the detection limit. We can assume that the oxidation process was finished and completely removed the pCBA. This result is in accordance with the result observed in table 3 at pH 4 and 6 mg/l of hydrogen peroxide.

Table 4: pCBA removal in time, pH 4 6  mg/l of hydrogen peroxide.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Feed (µg/l)</th>
<th>Concentrate (µg/l)</th>
<th>Permeate (µg/l)</th>
<th>pCBA conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>365</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>3</td>
<td>/</td>
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<td>11</td>
<td>97</td>
</tr>
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<td>/</td>
<td>&lt;5</td>
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<td>&gt;99</td>
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</tr>
<tr>
<td>30</td>
<td>/</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

3.2 Nanofiltration

3.2.1 pH 6 experiments

The figure 2 shows the results obtained at pH 6. The mass transfer coefficient ($K_{20}$) is plotted versus time. The calculation details of the mass transfer coefficient ($K_{20}$) are in appendix 7.3. The initial clean water curve was obtained by filtration of MilliQ water through the virgin membrane. The permeate flows decreased during the three experiments. However for the blank experiment without hydrogen peroxide, the decreasing is low and constant. On the opposite, for pH 6 with 2 mg/l hydrogen peroxide, the flow decreased rapidly during the first minute of the test and then get stable. A permeate flow decreasing is observed with 6 mg/l hydrogen peroxide however the variation is lower. The slopes of the decreasing part of both curves 2 and 6 mg/l of hydrogen peroxide seem to show that fouling occurred more rapidly for 2 mg/l of hydrogen peroxide than for 6 mg/l. However the measurements of the initial flows for the two oxidation experiments were not feasible, so the fouling behaviour is not confirmed. The hydrogen peroxide concentration seems to affect the membrane fouling which is higher at low peroxide concentration.
3.2.2 **pH 4 experiments**

The figure 3 shows the results obtained at pH 4. The mass transfer coefficient ($K_{20}$) is plotted versus time. The calculation details of the mass transfer coefficient are in appendix 7.3. The permeate flows decreased slowly and continuously during the three experiments. The slope of the curves is quite similar. In this experiment, the hydrogen peroxide concentration did not affect the membrane fouling.

At pH 4 and pH 6, the blank experiments had the same fouling behaviour. The flow decreased continuously. However the flow decreased more rapidly at pH 6. That suggests the fouling agent is more soluble in acid condition and the shapes of the curves during the oxidation experiments are different and are functions of the pH. Thus, the main fouling agent could be Fe$^{3+}$ because it is soluble at pH 4 and not at pH 6. In addition at pH 4 the Fenton catalytic cycle is more efficient and enables the back conversion of ferric iron to ferrous iron. Consequently less ferric irons were available to foul the membrane at pH4. Furthermore, the iso electric point of titanium oxide membrane is between 6 and 7, so the membrane was positively charge at pH 4. That can also have an effect on fouling by repulsion of the iron ions and iron hydroxide flocks.
Combination of Fenton oxidation process and ceramic nanofiltration

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Figure 3: \( K_{20} \) during oxidation experiments at pH 4

3.3 pCBA removal rate

Figure 4: \( K_{20} \) versus time for the Fenton process oxidation at pH 4 and 6 mg/l of H\(_2\)O\(_2\)
The trans-membrane coefficient ($K_{20}$) is plotted versus time in the figure 4. The calculation details of the trans-membrane coefficient are in appendix 7.3. The $K_{20}$ curve shows a rapid decreasing at the beginning of the run test and after 200 seconds, the $K_{20}$ values increased slowly. In addition, the curve of the oxygen concentration shows that the configuration of the pilot was not successful in keeping strictly anaerobic condition.

### 3.4 AOC measurements

The results for all samples are 0 µg C/l. This is due to a measurement problem, the bacteria inoculums died in all samples instead of growing. Consequently, no interpretation can be done with this result about AOC production during Fenton process.

### 3.5 Ions and salts passage

In table 5 the ion concentrations in feed, concentrate and permeate are shown. The samples of concentrate and permeate were collected after 25 minute of filtration under a feed pressure of 12 bars at 20°C.

<table>
<thead>
<tr>
<th></th>
<th>Feed concentration (mg/l)</th>
<th>Concentrate concentration (mg/l)</th>
<th>Permeate concentration (mg/l)</th>
<th>Salt rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3^-$</td>
<td>117</td>
<td>116</td>
<td>103</td>
<td>12</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>29.3</td>
<td>23.2</td>
<td>21.2</td>
<td>28</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>52.3</td>
<td>62.4</td>
<td>37.2</td>
<td>29</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>33</td>
<td>37</td>
<td>29</td>
<td>12</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>&lt; 4.5</td>
<td>&lt; 4.5</td>
<td>&lt; 4.5</td>
<td>-</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>12</td>
<td>13</td>
<td>&lt; 12</td>
<td>-</td>
</tr>
<tr>
<td>Fe total</td>
<td>8</td>
<td>7.8</td>
<td>5.9</td>
<td>26</td>
</tr>
</tbody>
</table>

A low salt rejection is observed, all percentages are below 30%. This nanofiltration membrane was not efficient to remove calcium, iron, bicarbonate and sulphate from the water. The removals of sodium and chloride were not expected by nanofiltration.
4 Conclusion and Recommendations

The combination of the Fenton oxidation process and ceramic nanofiltration has been investigated at the Waalwijk water treatment plant using anaerobic groundwater.
Based on the percentages of pCBA conversion, the Fenton process was effective with this type of water. OH radical formation was proved by the oxidation of the pCBA. The highest pCBA conversion occurred at pH=4 and high H₂O₂ concentration.
The ceramic nanofiltration membrane could withstand the highly oxidative environment without problems. However, rapid membrane fouling occurred (within minutes), it was probably due to iron(III) oxide precipitation.
The removal of ions was low (< 30%) under the experimental conditions used. It is expected that removal of organic micropollutants and their oxidation products will be low as well (Molecular Weight Cut-Off = 400 Da), but due to time constrictions and experimental difficulties this could not be verified.

According to the results which were obtained during this experiment, this system has a rising potential for the groundwater treatment but membranes with lower molecular weight cut-off are favourable. However these membranes are not commercially available yet. The application is not expected in the near future.

This experiment should be extended to investigate the efficiency of the combined Fenton process and ceramic nanofiltration system for micropollutant removals. Ceramic membrane having tighter pore size would be required to obtain higher ion removal and retention of micropollutants and oxidation products. The use of continuous membrane filtration will be convenient for the further investigation and the back-wash of the membrane will be applied to prevent ferric precipitates clogging the membrane.
5 List of references


6  Appendices

6.1  Pilot used
6.2 Flow diagram

6.3 $K_{20}$, trans membrane coefficient

$K_{20}$ is the mass transfer coefficient which is corrected according to the temperature (20°C). Based on the following formula the $K_{20}$ is calculated.

Water flux:

$$J_w = K_w (\Delta P - \Delta \Pi) = \frac{Q_p}{A} = \frac{1}{A} \frac{dV}{dt}$$

Where:
- $J_w = \text{water flux (L/m}^2\text{-hr)}$
- $K_w = \text{water mass transfer coefficient, (m/s.bar)}$
- $\Delta P = \text{transmembrane pressure differential, (bar)}$
- $\Delta \Pi = \text{transmembrane osmotic pressure differential, (bar)}$
- $Q_p = \text{permeate flow rate (L/hr)}$
- $A = \text{effective membrane area (m}^2\text{)}$
6.4 Membrane module