Disinfection of tertiary wastewater effluent prior to river discharge using peracetic acid; treatment efficiency and results on by-products formed in full scale tests

Per Overgaard Pedersen, Erling Brodersen and David Cecil

ABSTRACT

This is an investigation of chemical disinfection, with peracetic acid (PAA), in a tertiary sand filter at a full scale activated sludge plant with nitrification/denitrification and P-removal. The reduction efficiency of Escherichia coli and intestinal enterococci in the sand filter is reported. E. coli log reductions of between 0.4 and 2.2 were found with contact times from 6 to 37 min and with dosing from 0 to 4.8 mg L$^{-1}$. The average log reduction was 1.3. The decomposition products, bromophenols, chlorophenols and formaldehyde and residual H$_2$O$_2$ were measured before and after the sand filter. The residual H$_2$O$_2$ concentration in the effluent was critical at short contact times and high dosages of PAA due to the discharge limit of 25 μg L$^{-1}$. The other three products could not be detected at 0.1 μg L$^{-1}$ levels. The chemical cost of PAA dosing is estimated to be 0.039 US$ m$^{-3}$ treated wastewater.

Key words | by-products, disinfection, H$_2$O$_2$, peracetic acid, sand filter, wastewater

INTRODUCTION

Implementation of the EC Directive 2006/7/EC on the management of bathing water quality (henceforth the EC Directive) has increased focus in Europe on disinfection of wastewater effluents. Table 1 shows the quality requirements for inland waters as set forth in the EC Directive. Units are colony forming units (CFU) 100 ml. There are no limits for other bacteria, viruses or protozoa in the Directive.

The Municipality of Aarhus (Denmark), wants to use the harbour near the mouth of the Aarhus River for bathing. Therefore they require that the Aarhus River complies with the EC Directive for good quality inland waters (henceforth the agency) judged this insufficient to achieve good quality water in the Aarhus River. Therefore they asked Aarhus Water to plan for disinfection at the plant.

The Viby WWTP has a capacity of 83,000 person equivalents (PE) and an average daily flow of 13,000 m$^3$ d$^{-1}$. In wet weather the flow increases to 35,000 m$^3$ d$^{-1}$. The maximum hourly flow is 3,000 m$^3$ h$^{-1}$. The plant has fine screens and an aerated grit chamber, secondary treatment in an activated sludge A2/O-process with enhanced biological N- and P-removal and tertiary treatment in a rapid gravity, dual media sand filter.

The sand filter supplements the biological P-removal. The plant has a P discharge limit of 0.4 mg L$^{-1}$. The filter is divided into 14 cells. The sand depth is 1 m and the total volume is 370 m$^3$. FeClSO$_4$ (PIX 118, Kemira Ltd, Finland) is dosed in the influent. The dosage is 0.3 to 0.5 mg Fe L$^{-1}$. The filter is backwashed once a day at 3 am. A continuous backwashing cycle, in which one to four cells are backwashed in turn, is necessary when it rains.

In 2011, Aarhus Water investigated the performance of a sand filter, with Fe dosing but without chemical disinfection, at another but similar plant. The filter achieved an additional log reduction of 0.5 to 0.7 of Escherichia coli with respect to the plant’s secondary treatment (Pedersen 2011). The Viby WWTP’s licensing agency, the Aarhus Municipality, Department of Nature and Environment (henceforth the agency) judged this insufficient to achieve good quality water in the Aarhus River. Therefore they asked Aarhus Water to plan for disinfection at the plant.
Previously, Pedersen (2010) explored the feasibility of disinfection using peracetic acid (PAA) prior to the Viby WWTP’s sand filter and UV after the sand filter. Table 2 shows cost estimates computed in this study. Literature on a number of investigations of disinfection with PAA in water filled contact chambers (Stampi et al. 2001; Kitis 2004) was found but no studies of PAA dosing in a sand filter. A combination of PAA and UV (González et al. 2012) was not considered. Other methods of chemical disinfection were not considered because of concerns about worker safety and harmful by-products.

Based on this study, Aarhus Water proposed PAA dosing before the sand filter. In reply, the agency proposed an average H2O2 discharge limit of 10 µg L⁻¹ and a maximum limit of 25 µg L⁻¹. These limits follow a European requirement that a discharge must not result in more than a 10 µg L⁻¹ increase in the H2O2 concentration in the receiving waters. Furthermore chlorophenols, bromophenols and formaldehyde were identified as possible harmful by-products from PAA disinfection. Therefore, the agency requested that three effluent samples be analysed for these three compounds. However, no discharge limits on these compounds were proposed.

The agency did not propose discharge limits on E. coli or intestinal enterococci (henceforth enterococci). They assumed that PAA disinfection combined with dilution and residence time in the river would ensure good quality water at the mouth of the Aarhus River. At the same time, there is an agreement with the municipality that bathing will be forbidden during and after combined sewer overflows.

In this investigation, the use of PAA was tested at the Viby WWTP in full scale over a 3½-month period.

**METHODS**

DEGACLEAN®, a PAA produced by Evonik Industries AG, Germany, was dosed in the inlet distribution channel to the sand filter. This is an equilibrium mixture of PAA, H2O2, acetic acid and water where PAA is at least 14% by weight. From a 25 m³ storage tank, a pump dosed a fixed volume of the product on a pulse command. Pulses were sent to the pump in proportion to the effluent flow from the sand filter. The PAA was mixed into the secondary treated wastewater by a Statiflo Series 900 Channel Mixer (Statiflo International Ltd, UK) installed in the distribution channel to the sand filter.

Contact time was computed on the basis of the filter volume (not the pore volume). The volume of filter cells out of operation due to a backwash cycle was not included.

**Sampling**

Twenty-six sets of samples of the sand filter influent and effluent were collected. As a rule, two sample sets were taken each week on random work days and at random times during normal working hours. Each sample was a composite of five grab samples collected over a period of 5 min according to the agency’s specifications. The grab samples were mixed to one sample and stored in a sterile bottle. Sample sets were numbered in chronological order.

Nine sample sets were collected in the Aarhus River. These samples were taken at the same time as nine of the 26 sets. One sample was collected 50 m upstream from the plant effluent and a second sample was collected 70 m downstream. Both samples were collected 1 m from the river bank.

**Microbiological analyses**

At the plant, all of the samples were analysed for E. coli using 3M™ Petrifilm™ Select E. coli Count Plates incubated for 24 h at 42 ± 2°C (3M Inc. 2015). At Analytech Miljølaboratorium A/S Denmark, five of the 26 sample sets were analysed for both E. coli and enterococci, according to the standard methods ISO 9308-3 and ISO 7899 respectively.

---

**Table 1 | The EC Directive for bathing water quality in inland waters, CFU 100 mL⁻¹**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Excellent</th>
<th>Good</th>
<th>Sufficient</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intestinal enterococci</td>
<td>200 (a)</td>
<td>400 (b)</td>
<td>330 (a)</td>
<td>ISO 7899-1 or 2</td>
</tr>
<tr>
<td>E. coli</td>
<td>500 (a)</td>
<td>1,000 (b)</td>
<td>900 (a)</td>
<td>ISO 9308-1 or 3</td>
</tr>
</tbody>
</table>

*aBased on a 90-percentile evaluation.
*bBased on a 95-percentile evaluation.

**Table 2 | Estimated costs for disinfection at the Viby WWTP**

<table>
<thead>
<tr>
<th>PAA (mill. US$)</th>
<th>UV (mill. US$)</th>
<th>Power and lamps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment</td>
<td>Investment</td>
<td>Total Chemical</td>
</tr>
<tr>
<td>0.42</td>
<td>2.33</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
</tr>
</tbody>
</table>

*aIncluding maintenance and depreciation of investment costs over a 15-year lifetime.
Residual H$_2$O$_2$

H$_2$O$_2$ was measured at the plant in 23 of the 26 sample sets and all nine of the sample sets from the Aarhus River. H$_2$O$_2$ was determined by a photometric method in which N,N-diethyl-p-phenylenediamine (DPD) is oxidized by a peroxidase catalysed reaction (Bader et al. 1988). The detection limit varied between 5 and 10 μg L$^{-1}$.

Furthermore, on 1 day seven extra samples of the effluent from the sand filter were collected specifically for residual H$_2$O$_2$ measurements. These samples were assigned letters A to G.

By-products

Three sample sets were analysed for the by-products chlorophenols (analytical method: DIN EN 12673, detection limit 0.1 μg L$^{-1}$), bromophenols (analytical method: DIN EN 12673, detection limit 0.1 μg L$^{-1}$) and formaldehyde (analytical method: SOP QMA-M 3-42, detection limit 0.1 μg L$^{-1}$) by GBA Gesellschaft für Bioanalytik mbH, Hildesheim, Germany.

RESULTS

Table 3 shows five of the 26 E. coli counts for influent and effluent samples. The results are ordered by the effluent count and the five values lie above the good quality concentration of 1,000 CFU ml$^{-1}$. It can be concluded that PAA dosing up to the maximum in this investigation will not insure a good quality effluent for bathing. However, as mentioned above, the plant’s proposed discharge permit does not include limits on E. coli or enterococci.

Table 3 | High E. coli counts to and from the sand filter

<table>
<thead>
<tr>
<th>Sampling no.</th>
<th>Contact time min</th>
<th>PAA dosing mg L$^{-1}$</th>
<th>Influent CFU 100 ml$^{-1}$</th>
<th>Effluent CFU 100 ml$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Petrifilm</td>
<td>ISO</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>4.0</td>
<td>14,000 1,500</td>
<td>1,100 860</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>4.0</td>
<td>45,000 13,000</td>
<td>1,200 1,900</td>
</tr>
<tr>
<td>11</td>
<td>32</td>
<td>4.0</td>
<td>60,000 a</td>
<td>1,400 a</td>
</tr>
<tr>
<td>18</td>
<td>15</td>
<td>4.8</td>
<td>32,000 a</td>
<td>1,500 a</td>
</tr>
<tr>
<td>23</td>
<td>35</td>
<td>4.8</td>
<td>260,000 a</td>
<td>1,800 a</td>
</tr>
</tbody>
</table>

*No analysis performed.

The log log correlation between all 10 Petrifilm™ and ISO counts for the same samples was:

\[
\log(y) = 0.9518 \log(x) + 0.0206, \quad R^2 = 0.79
\]

where \(x\) is the Petrifilm™ count and \(y\) is the result predicted for an ISO count. By removing one outlier, the combination of 14,000 measured with Petrifilm™ and 1,500 measured by the ISO standard shown in the first row of Table 3, the log log correlation improves to \(R^2 = 0.89\). In other words, Petrifilm™ counts gave a good estimate of the ISO count.

Table 4 shows the enterococci counts done according to ISO standard. Due to a mechanical failure no PAA was dosed on 2 days when sample sets were collected. The log reductions with dosing indicate that PAA is just as effective against enterococci as E. coli.

Only one of the nine sample sets collected in the Aarhus River showed a significant increase in the E. coli count after the plant effluent. The effluent count was 3,800 CFU 100 mL$^{-1}$ and the up and downstream counts were 100 and 800 respectively. The 700 CFU 100 mL$^{-1}$ increase agrees well with a 1:4 dilution based on the average flows of the effluent and the river. The effluent counts associated with the other eight river sample sets were at or below 1,100 CFU 100 mL$^{-1}$.

Table 5 shows seven of the 30 measurements of H$_2$O$_2$ in the effluent from the sand filter. These seven are all at or above the plant’s average discharge limit of 10 μg L$^{-1}$ and three are above the maximum limit of 25 μg L$^{-1}$.

Table 5 also shows two of the eight sample sets from the Aarhus River. The agency assumes that the high H$_2$O$_2$ concentrations in the 50 m upstream samples are the result of sunlight reacting with organic matter in Brabrand Lake. This process is observed in lakes in Finland (Häkkinen et al. 2004).

All results from the analyses of the bromophenols, chlorophenols and formaldehyde were less than 0.1 μg L$^{-1}$, the detection limit of the analysis methods. There should

Table 4 | Enterococci counts to and from the sand filter

<table>
<thead>
<tr>
<th>Sampling no.</th>
<th>Contact time min.</th>
<th>PAA dosing mg L$^{-1}$</th>
<th>Influent ISO CFU 100 ml$^{-1}$</th>
<th>Effluent ISO CFU 100 ml$^{-1}$</th>
<th>Log reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15</td>
<td>4.0</td>
<td>8,600</td>
<td>38</td>
<td>2.4</td>
</tr>
<tr>
<td>9</td>
<td>18</td>
<td>4.0</td>
<td>1,000</td>
<td>130</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>17</td>
<td>3.2</td>
<td>5,200</td>
<td>460</td>
<td>1.1</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>0.0</td>
<td>39,000</td>
<td>1,000</td>
<td>1.6</td>
</tr>
<tr>
<td>7</td>
<td>12</td>
<td>0.0</td>
<td>51,000</td>
<td>16,000</td>
<td>0.5</td>
</tr>
</tbody>
</table>
The two sample sets collected when there was no dosing of PAA were not included in the fit. However, they are shown as two points on the Y-axis. These results are similar to the results shown in Kitis (2004) with respect to the poor correlation between CT and reduction. However, they are in the lower end of the range for secondary wastewater. This indicates that the action of the sand compensates in part for the reduction in true contact time relative to a water filled contact chamber. On the other hand, Koivunen & Heinonen-Tanski (2005) showed consistently better reductions for secondary effluent with PAA dosing in a water filled chamber.

Based on Azzellino et al. (2011) a multivariate model was computed for the log of the E. coli count in the effluent, log \( n_e \). The model is:

\[
\log(n_e)_{\text{predicted}} = 0.70 \log(n) - 0.19C - 0.012T + 1.11, \quad R^2 = 0.75
\]  

(3)

The two sample sets collected when there was no dosing of PAA were included in this fit because the model permits zero values for \( C \). The model parameters were computed using the multiple linear regression function in the Excel\textsuperscript{TM} spreadsheet. A data and parameter analysis (Brereton 2003) showed that log(\( n \)) was more significant than \( C \) and \( C \) was much more significant than \( T \).

**Residual H\textsubscript{2}O\textsubscript{2}**

Figure 2 shows the effluent H\textsubscript{2}O\textsubscript{2} concentration as a function of \( C/T \). Triangles mark the results for the seven effluent samples collected on 1 day specifically for residual H\textsubscript{2}O\textsubscript{2}. \( C/T \) greater than 0.26 mg L\textsuperscript{-1} min\textsuperscript{-1} resulted in concentrations greater than 25 μgL\textsuperscript{-1}, the plant’s discharge

### DISCUSSION

**E. coli log reductions in the sand filter**

Figure 1 shows the log reduction of E. coli as a function of CT, the PAA dose (C) times the contact time (T). \( n \) is the influent count and \( n_e \) is the effluent count (CFU 100 ml\textsuperscript{-1}). Only counts measured on Petrifilm\textsuperscript{TM} were used. The average log reduction was 1.3.

The fitted function in Figure 1 is:

\[
\log(n/n_e) = 0.27 \ln(CT) + 0.12, \quad R^2 = 0.29
\]  

(2)

### Table 5 | Critical H\textsubscript{2}O\textsubscript{2} effluent concentrations

<table>
<thead>
<tr>
<th>Sampling no.</th>
<th>Contact time min</th>
<th>PAA dosing mg L\textsuperscript{-1}</th>
<th>Plant effluent µgL\textsuperscript{-1}</th>
<th>Aarhus River 50 m up µgL\textsuperscript{-1}</th>
<th>70 m down µgL\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>37</td>
<td>4.8</td>
<td>10</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>4.0</td>
<td>12</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>D</td>
<td>13</td>
<td>4.0</td>
<td>12</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>11</td>
<td>4.0</td>
<td>12</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>1.6</td>
<td>36</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>14</td>
<td>7</td>
<td>2.4</td>
<td>38</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>4.0</td>
<td>69</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

<sup>a</sup>No sample was collected.
limit. Based on these results Aarhus Water plans to use the following dosing control algorithm:

If $T > 14$ min, then $C = 3.6 \text{ mg L}^{-1}$
If $14 < T < 9$, then $C = 0.26 T$
If $T < 9$, then $C = 0$.

$T$ will be computed online based on the flow and the number of filter cells in use.

**Chemical costs**

Currently the availability of PAA is limited and the cost in Europe is ca. 1,800 US$ ton$^{-1}$ for bulk delivery of 14% PAA. Based on the control algorithm above and the recorded flows to the plant, the chemical costs are estimated to be 0.039 US$ m$^{-3}$ wastewater. This is slightly higher than the estimated chemical cost shown in Table 2 because the price of PAA has increased since the first estimate was made.

**CONCLUSIONS**

This study demonstrates full-scale PAA disinfection of wastewater in a tertiary sand filter. With a PAA-dosing ($C$) of 0 to 4.8 mg L$^{-1}$ and contact times ($T$) between 6 and 37 min, the $E. coli$ log reduction was between 0.4 and 2.2. The average was 1.3. This is an improvement over the 0.5 to 0.7 log reductions observed in a similar filter without PAA dosing.

Three sets of influent and effluent samples were analysed for the by-products bromophenols, chlorophenols and formaldehyde. All results were less than 0.1 $\mu$g L$^{-1}$, the detection limit of the analysis methods. This supports the conclusion that by-products of PAA dosing are less harmful than the by-products of other methods of chemical disinfection.

The residual $\text{H}_2\text{O}_2$ in the effluent is critical due to the WWTP's discharge limit of 25 $\mu$g L$^{-1}$. $C/T$ greater than 0.26 mg L$^{-1}$ min$^{-1}$ resulted in residual $\text{H}_2\text{O}_2$ concentrations greater than 25 $\mu$g L$^{-1}$. For this reason a control strategy will be used in which $C$ is constant at 3.6 mg L$^{-1}$ for $T > 14$ min. For $T < 14$ min, $C$ will be 0.26 $T$. For $T < 9$ min, $C$ will be 0.

The chemical cost, based on this control strategy and the 2013 price for PAA, is 0.039 US$ m$^{-3}$ of treated wastewater.

**REFERENCES**

3M Inc. 2013 analysis procedure available online at http://solutions.3m.co.uk/3MContentRetrievalAPI/BlobServlet?lmd=1357828352000&locale=en_GB&assetType=MMM_Image&assetId=1319245354361&blobAttribute=ImageFile (accessed 2 June 2013).


