METHANOL DOSING TRIAL FOR ENHANCED DENITRIFICATION AT LILYDALE STP

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**ABSTRACT**

Under EPA Discharge Licenses, Yarra Valley Water discharges STP effluent to stream which eventually flows via the Yarra River to Port Philip Bay. Nutrient loads in streams and in Port Philip Bay are an ongoing issue and methods of reducing these loads are continually being investigated. One method of reducing the nutrient loads in the bay is to decrease the levels of nutrients entering the water networks through upstream discharges. During late summer and autumn 2008 a methanol dosing trial was conducted at Lilydale STP to assess the possibility of using methanol for enhanced denitrification. A total nitrogen limit of 10 mg/L is in place at the plant and under normal operation effluent total nitrogen levels of 4.5 to 7 mg/L are generally achieved. This paper outlines the procedure used to dose the methanol during the trial period, the sampling regime undertaken to compare nutrient levels in dosed with un-dosed effluent and any process impacts or changes observed while methanol was being dosed at the STP. Results of the trial showing a 40% reduction in total nitrogen levels are also detailed in this paper.

**KEY WORDS**

Denitrification, Methanol, Total Nitrogen, Nitrate, Sand Filter, Solids

**1.0 INTRODUCTION**

In late 2004, it was agreed between EPA Victoria and Yarra Valley Water that an enhanced denitrification trial be conducted at a Yarra Valley Water sewage treatment plant (STP).

Denitrification in wastewater treatment is the process by which nitrates in the process stream are broken down into nitrogen gas in the presence of specific denitrifying bacteria. Optimum denitrification by these bacteria is achieved in anoxic conditions with a readily available carbon rich food source. Anoxic conditions predominantly prevail in the sand filters and methanol is known to provide a good source of readily bio-available carbon. Therefore, it was decided that the denitrification trial to be conducted would be the dosing of methanol onto a sand filter system. Lilydale STP employs a biological nutrient reactor (BNR) treatment system with upfront screening followed by sand filters and ultraviolet disinfection. The plant generally produces consistent quality effluent with total nitrogen levels between 4.5 to 7 mg/L and is the second largest plant operated by YVW. Due to these attributes, Lilydale STP was chosen as the site at which the denitrification trial would be conducted.

The objectives of the methanol dosing trial were to:

- Determine the effectiveness of dosing methanol into the sand filters with respect to greater levels of nitrogen removal within the treatment plant
- Assess any process impacts/side effects of the methanol dosing
- Provide an understanding of the effects of methanol dosing on the treatment process
- Determine some recommendations as to the long term viability of such a scheme.
In 2007, a methanol storage and dosing facility was constructed at Lilydale STP in order to conduct this trial. The methanol dosing trial commenced on the morning of Monday 25\textsuperscript{th} Feb 2008, with the aim to run the trial over an 8 week period.

During the trial, methanol was dosed at a rate of 11 mg/L, into two of the four sand filter cells. A dose rate of 11 mg/L was based on an average effluent nitrate concentration of 4.5 mg/L, a target effluent nitrate concentration of 1 mg/L and a methanol requirement of 3.2 kg methanol per kg of nitrate [1]. Samples were collected throughout the trial period and analysed in accordance with the sampling program as follows:

- Filter Influent & Effluent (effluent x 4) from each individual cell
  - NO\textsubscript{3} twice per day during the week and once per day on the weekend
  - TN & TKN once per day everyday
  - NH\textsubscript{3} and NO\textsubscript{2} weekly

- Filter Effluent
  - COD on alternating days from cells 1 & 2 and cells 3 & 4 for the duration of the trial period

2.0 RESULTS

Samples were collected according to the sampling program outlined above and analysed by Ecowise Environmental. Tables 1 and 2 show sampling results for nitrates and total nitrogen respectively for selected samples throughout the trial period, giving a representation of the data obtained. Cells 1 and 3 were dosed with methanol. Cells 2 and 4 were not. Observation of the results in Table 1 shows a significant reduction in nitrate concentrations in the dosed effluent samples over the trial period, compared to influent and un-dosed effluent samples.

\begin{table}[h]
\centering
\caption{Nitrate sampling results in mg/L}
\begin{tabular}{|c|c|c|c|c|}
\hline
Sample No. & Influent & Cell 1 Effluent (Methanol dosed) & Cell 2 Effluent & Cell 3 Effluent (Methanol dosed) & Cell 4 Effluent \\
\hline
25 Feb Sample 1 & 4.4 & 5.5 & 5.1 & 4.9 & 2.2 \\
29 Feb Sample 1 & 5.2 & 6.4 & 6.3 & 8.5 & 6.1 \\
4 Mar Sample 2 & 2.8 & 2.1 & 3.2 & 1.9 & 3.2 \\
12 Mar Sample 2 & 4.2 & 2.3 & 4.1 & 2.1 & 4.2 \\
19 Mar Sample 1 & 0.54 & 0 & 0.54 & 0 & 0.56 \\
27 Mar Sample 1 & 1.9 & 0.01 & 1.8 & 0.01 & 1.5 \\
1 Apr Sample 1 & 4 & 3.8 & 4.6 & 3.6 & 5.5 \\
9 Apr Sample 2 & 3.8 & 0.98 & 3.2 & 1.6 & 2.8 \\
14 Apr Sample 2 & 4.3 & 1.9 & 5 & 1.9 & 4.9 \\
20 Apr Sample 1 & 4.2 & 1.9 & 6.2 & 1.8 & 4.3 \\
Median & 4.1 & 2 & 4.4 & 1.9 & 3.7 \\
\hline
\end{tabular}
\end{table}

As per table 1, observation of table 2 below shows a reduction in total nitrogen concentrations in the dosed effluent samples over the trial period, compared to influent and un-dosed effluent samples, although this reduction is not as marked as the nitrate reduction.
Table 2:  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Influent</th>
<th>Cell 1 Effluent</th>
<th>Cell 2 Effluent</th>
<th>Cell 3 Effluent</th>
<th>Cell 4 Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 Feb Sample 2</td>
<td>4.5</td>
<td>4.2</td>
<td>4.7</td>
<td>4.5</td>
<td>4.6</td>
</tr>
<tr>
<td>29 Feb Sample 2</td>
<td>5.3</td>
<td>5.9</td>
<td>5.5</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>4 Mar Sample 2</td>
<td>4.2</td>
<td>3.2</td>
<td>4</td>
<td>2.7</td>
<td>4.2</td>
</tr>
<tr>
<td>12 Mar Sample 2</td>
<td>5.6</td>
<td>3.7</td>
<td>5.1</td>
<td>3.3</td>
<td>5.3</td>
</tr>
<tr>
<td>19 Mar Sample 2</td>
<td>4.2</td>
<td>3.2</td>
<td>4.9</td>
<td>3</td>
<td>4.7</td>
</tr>
<tr>
<td>27 Mar Sample 2</td>
<td>3.9</td>
<td>2.2</td>
<td>3.5</td>
<td>1.8</td>
<td>3.4</td>
</tr>
<tr>
<td>1 Apr Sample 2</td>
<td>6.3</td>
<td>5</td>
<td>6.1</td>
<td>4</td>
<td>6.2</td>
</tr>
<tr>
<td>9 Apr Sample 2</td>
<td>5.3</td>
<td>2.4</td>
<td>4.1</td>
<td>2.9</td>
<td>3.8</td>
</tr>
<tr>
<td>14 Apr Sample 2</td>
<td>6.2</td>
<td>3.6</td>
<td>6.1</td>
<td>3.5</td>
<td>5.9</td>
</tr>
<tr>
<td>20 Apr Sample 1</td>
<td>9.1</td>
<td>3.8</td>
<td>8.2</td>
<td>3.3</td>
<td>5.4</td>
</tr>
<tr>
<td>Median</td>
<td>5.3</td>
<td>3.7</td>
<td>5.0</td>
<td>3.3</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Only the results from the nitrate and total nitrogen analysis have been shown as TKN, NO₂ and NH₃ appeared relatively unaffected through the addition of methanol, as expected. COD concentrations measured in the filter cell effluent streams varied quite a lot during the trial period, from a minimum of 7 mg/L to a maximum of 61 mg/L and an average of 27 mg/L. However, there was no clear correlation between the observed COD concentrations and the addition of the methanol as the results varied to the same degree and in the same range in the dosed cells as the un-dosed cells. This suggests all the methanol was consumed in the sand filters.

Figures 1 and 2 below compare the differences between the sand filter influent and effluent nitrate and influent and effluent total nitrogen concentrations respectively, for both the dosed and un-dosed filter cells.

Figure 1:  

Percentage reduction in nitrates across filter cells
After 2 weeks of methanol dosing, a significant reduction in nitrate levels across the dosed cells can be seen. Although not affected as markedly as the dosed cells, the undosed cells also show some trend over the trial period. As with the dosed cells, at the beginning of the trial, there is virtually no denitrification observed across the un-dosed cells. As the trial progresses, the variance in nitrogen levels across these cells levels off, and a slight trend towards a reduction in nitrogen concentrations emerges. This suggests that there may have been a carry-over of denitrifying bacteria into the un-dosed cells through the backwash process.

3.0 DISCUSSION

Analysing the results that have been collated, it can be seen that there was a steady reduction in nitrate concentrations in the dosed effluent compared to the un-dosed effluent over the trial period. The nitrate concentrations analysed in the dosed effluent were up to 100% less than that of the effluent from the un-dosed cells in some instances, where the nitrate concentration was reduced to 0 mg/L across the dosed filter cells. This reduction in nitrates led to the total nitrogen concentrations analysed in the effluent from dosed cells being up to 60% less than effluent from un-dosed cells.

3.1 Nitrogen Reduction

Average total nitrogen concentration in the dosed effluent over the trial period was 3.6 mg/L, with the average total nitrogen concentration in the un-dosed effluent being 5.2 mg/L. These figures can be compared with an average effluent total nitrogen concentration of 7.8 mg/L over 2006/07. Although the trial was only conducted over an 8 week period, results indicate that the introduction of methanol onto the sand filters does reduce nitrogen levels in the effluent stream, through enhanced denitrification. This observation is in line with literary and theoretical suggestions that denitrifying bacteria will prosper in an anoxic environment, such as exists through the sand filters, in the presence of readily available carbon food source.
The bacteria in the sand filters consume the oxygen bound to nitrogen in nitrates through respiration in the production of energy. However, in order for the bacteria to respire, there needs to be a food source available. Once there is ample food available, the bacteria will continue to respire, thereby consuming the oxygen bound in the form of nitrates to release nitrogen gas with the net effect of reducing nitrogen in the effluent stream.

As mentioned in the results section above, no obvious trend was seen in the COD data obtained over the course of the trial period. The COD was found to vary significantly and to the same degree in both the dosed and the undosed effluent streams. Final effluent sampling also shows BOD in the STP effluent to be similar before, during and after the trial period. Therefore, from the data obtained over this trial, it cannot be said that the addition of methanol to the process had an effect on the effluent stream COD or BOD.

3.2 Sand Filter – Operational Impacts

With this increased bacteriological activity in the sand filters, there would be an expected increase in the level of fouling in the filters. In order therefore, to maintain a reasonable flux rate that allows throughput of the filters to keep up with plant flows, more frequent backwashing of the filters might be required. Over the 8 week trial period, an increase in the frequency of backwashes was not noticed. However, backwashes are automatically instigated by the differential pressure and therefore their frequency may have increased slightly over the trial. In any case, it would be reasonable to say that in the long term, the frequency of backwashing in the sand filters could increase with continued methanol dosing, although the degree by which it might increase is largely unknown.

3.3 Solids Production

A side-effect of the methanol dosing that was noticed was an increase in solids generated in the treatment process. It is believed that this increase in solids generation is due to greater biomass growth on the filters, leading to an increase in biomass being transferred back to the treatment tanks through the backwashing of the filters. In order to maintain an optimum solids level in the treatment tanks, sludge is regularly wasted from the treatment tanks. During the methanol dosing trial, the volume of sludge wasted increased by an average of 6% to prevent the solids reaching too high a concentration. This in turn means there would be an extra 6% of waste sludge generated from the treatment process which must be managed and either re-used or stockpiled as is currently the case. Even with the increased wasting, the solids concentration in the aeration tanks still rose by almost 20%. However, this increase in suspended solids was not detrimental to the treatment process and stabilised after the initial 4 to 5 weeks of the trial. However, as the concentration of biomass and suspended solids increased in the treatment tank and sand filters, and the levels of biological activity in the filters increased, there was no obvious decline in effluent quality. This shows that the sand filtration and UV disinfection adequately coped to remove or inactivate the increased loading.

4.0 CONCLUSION

In conclusion, it can be stated that the dosing of methanol into the sand filters did prove effective in reducing the levels of nitrogen in the effluent stream and it was clearly demonstrated that the addition of methanol does enhance denitrification, with an average reduction in total nitrogen of 2.1 mg/L after the initial two weeks of the trial period.
The average reduction in nitrate after the initial two weeks was 1.9 mg/L, which is very similar to the reduction in total nitrogen as expected. This reduction is however, less than that expected based on the theoretical rate of 1 mg of nitrate removed per 3.2 mg of methanol dosed. At the methanol dose rate of 11 mg/L and the theoretical stoichiometric reduction rate, a nitrate reduction of 3.4 mg/L should have been observed. A possible reason for not removing the expected 3.4 mg/L of methanol may be the consumption of methanol by other compounds in the effluent stream or perhaps temperature effects, affecting the reaction rates of the denitrification process. The trial was not conducted over a long enough period to assess seasonal effects.

However, there are side effects associated with the methanol dosing such as increased solids generation in the treatment tanks and subsequent sludge wasting from the process. Nevertheless, these side effects are controllable with adequate management procedures in place.

What must be taken into consideration, when assessing the long term application of such a scheme is the cost of the scheme both financially and environmentally. Financially, the impacts of such a scheme are quite obvious, with the extra cost associated with purchasing methanol, extra energy required with regard to solids wasting and sludge handling as well as the initial capital cost of establishing such a facility. Based on the removal rate of nitrogen observed in this trial, the unit cost of nitrogen removal was 0.9 cent per mg (methanol cost of $1.66/kg). This cost takes into account the procurement of methanol only and does not consider extra energy or other operational cost. In environmental terms, there may be cost savings with lower nitrogen loads being released to stream, however, this decreases the nutritional value of the effluent if recycled for use in an irrigation scheme as well as extra power consumption in solids wasting and truck movements which may have a negative environmental impact.

There are also management and control procedures which must be implemented if methanol is used at STP sites as it is a toxic and highly flammable compound. All storage and transfer equipment must be adequately earthed to prevent static build-up and all electrical or mechanical equipment used in the vicinity of the methanol must be intrinsically safe to remove all ignition sources.

Overall, the field test data is conclusive with regard to the positive effects of methanol addition to the denitrification process in the tertiary filters.

5.0 ACKNOWLEDGEMENTS

Valuable contributions were made by all management and staff of all organisations involved. In particular Chris Brace of YVW did a lot of work in the preparation of the trial and construction of the dosing facility, which was constructed by PMP Environmental Pty Ltd. The YVW Operations staff, in particular Daryl Haag and Shane Smith, at Lilydale STP must be acknowledged for the extra work load they took on during the trial period, conducting regular monitoring, sampling and checking plant performance throughout the trial. Also the other YVW Operators in the Eastern area who carried out rostered and out-of-hours sampling for analysis by Ecowise Environmental are due a mention.

6.0 REFERENCES