Development and optimisation of VFA driven DEAMOX process for treatment of strong nitrogenous anaerobic effluents

S. V. Kalyuzhnyi, M. A. Gladchenko, Ho Kang, A. Mulder and A. Versprille

ABSTRACT

The recently proposed DEAMOX (DEnitrifying AMmonium OXidation) process combines the anammox reaction with autotrophic denitrifying conditions using sulphide as an electron donor for the production of nitrite from nitrate within an anaerobic biofilm. This paper firstly presents a feasibility study of the DEAMOX process using synthetic (ammonia + nitrate) wastewater where sulphide is replaced by volatile fatty acids (VFA) as a more widespread electron donor for partial denitrification. Under the influent N-NH$_4^+$/N-NO$_3^-$ and COD/N-NO$_3^-$ ratios of 1 and 2.3, respectively, the typical efficiencies of ammonia removal were around 40% (no matter whether a VFA mixture or only acetate were used) for nitrogen loading rates (NLR) up to 1236 mg N/l/d. This parameter increased to 80% by increasing the influent COD/N-NO$_3^-$ ratio to 3.48 and decreasing the influent N-NH$_4^+$/N-NO$_3^-$ ratio to 0.29. As a result, the total nitrogen removal increased to 95%. The proposed process was further tested with typical strong nitrogenous effluent such as reject water from anaerobic digestion. For this, the raw wastewater was split and partially (50%) fed to a nitrifying reactor (to generate nitrate) and the remaining part (50%) was directed to the DEAMOX reactor where this stream was mixed with the nitrified effluent. Stable process performance up to NLR of 1,243 mg N/l/d in the DEAMOX reactor was achieved resulting in 40, 100, and 66% removal of ammonia, NO$_x^-$, and total nitrogen, respectively.

Key words | anammox, DEAMOX, heterotrophic denitrification, nitrogen removal, VFA

INTRODUCTION

Thermophilic anaerobic digestion of a mixture of primary and secondary sludge has traditionally been used at Moscow municipal wastewater treatment plants (WWTP) since the 1950s (Khramenkov et al. 2003). Reject water from digested sludge dewatering contains significant amount of nitrogen (Table 1) and is currently returned back to the head of WWTPs, increasing the total nitrogen load by 10–20%. Since Moscow sewage has a BOD deficiency to fulfil denitrification requirements (Khramenkov et al. 2005) there is a strong need for development of other methods of nitrogen removal from this stream.

A new biological nitrogen removal process called DEAMOX (DEnitrifying AMmonia OXidation) for treatment of strong nitrogenous wastewater has been recently proposed (Kalyuzhnyi et al. 2006). It combines the anammox reaction with autotrophic denitrifying conditions using sulphide as an electron donor for the production of nitrite from nitrate within an anaerobic biofilm:

\[
\begin{align*}
\text{NO}_3^- + 0.25\text{HS}^- & \rightarrow \text{NO}_2^- + 0.25\text{SO}_4^{2-} + 0.25\text{H}^+ \\
\text{NH}_4^+ + \text{NO}_2^- & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Since the standard application of this process is restricted to sulphur bearing wastewater, the first objective of this paper was to perform a feasibility study of the process...
DEAMOX process using synthetic (ammonia + nitrate) wastewater under replacement of sulfide by volatile fatty acids (VFA) as a more widespread electron donor (e.g., as in reject water, Table 1) for partial denitrification:

\[
\begin{align*}
\text{NO}_2^- + 0.25\text{CH}_3\text{COO}^- &\rightarrow \text{NO}_2^- + 0.25\text{HCO}_3^- \\
&+ 0.25\text{CO}_2 + 0.25\text{H}_2\text{O} 
\end{align*}
\] (1a)

The second objective of the paper was to test the developed VFA driven DEAMOX process with real reject water after thermophilic sludge anaerobic digestion from Moscow WWTP (Table 1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7 – 8.0</td>
<td>Total N, mg N/l</td>
<td>530 – 566</td>
</tr>
<tr>
<td>Total COD, mg/l</td>
<td>1,140 – 1,780</td>
<td>Ammoniac N, mg N/l</td>
<td>320 – 444</td>
</tr>
<tr>
<td>Soluble COD, mg/l</td>
<td>660 – 850</td>
<td>Phosphate P, mg P/l</td>
<td>10 – 11</td>
</tr>
<tr>
<td>VFA, mg COD/l</td>
<td>500 – 650</td>
<td>Sulphate, mg/l</td>
<td>15 – 18</td>
</tr>
<tr>
<td>Alkalinity_{pH 4.5}, meq/l</td>
<td>29 – 31</td>
<td>Sulphide, mg/l</td>
<td>4 – 5</td>
</tr>
</tbody>
</table>

Treatment of reject water. The raw wastewater was split and ~ 50% of flow was fed to a nitrifying reactor (to generate nitrate) and the remaining part was directed to the DEAMOX reactor where this stream was mixed with the nitrified effluent. The DEAMOX reactor was the same as described in the previous section and contained the sludge developed during the experiments with synthetic wastewater. As a nitrifying unit, a laboratory activated sludge reactor with internal settler (rectangular cross-section 283 cm², height 12 cm and total working volume 3.42 – 4.35 l) was operated under ambient temperature of the laboratory (20 ± 3°C). 1.5 – 2.5 g/l of NaHCO₃ was added to the influent of this reactor to compensate for the lack of alkalinity of reject water fed (Table 1) and to ensure complete nitrification. The dissolved oxygen concentrations were maintained above 2 mg/l throughout the study. The nitrifying sludge from the previous study (Kalyuzhnyi et al. 2006) was used as a seed. The excess of sludge produced was periodically (usually 40 – 60 ml per 2 – 3 weeks) withdrawn from the reactor.

Analyses. All analyses were performed as described previously (Kalyuzhnyi et al. 2006).

RESULTS AND DISCUSSION

Start-up of the DEAMOX reactor with synthetic wastewater

The required COD/N-NO₃⁻ ratio for partial denitrification (reaction 1a) with taking into account the COD expenses for biomass growth (0.4 g biomass-COD/g COD, Henze et al. 1997) is 1.9. However, if denitrification of nitrite proceeds further, i.e., according to the reaction:

\[
\begin{align*}
\text{NO}_2^- + 0.375\text{CH}_3\text{COO}^- + 0.625\text{H}^+ &\rightarrow -0.5\text{N}_2 + 0.75\text{HCO}_3^- + 0.5\text{H}_2\text{O} 
\end{align*}
\] (1b)

the required COD/N-NO₃⁻ ratio (using the same biomass growth yield) increases to 4.76. Since reaction 1b is highly undesirable for the VFA driven DEAMOX process, the influent COD/N-NO₃⁻ ratio was maintained close to the minimal required value (~ 2.3) during the start-up period. After 1.5 months of running of the VFA driven DEAMOX reactor with the average nitrogen loading rate (NLR) of 207 mg N/l/d (average hydraulic retention time (HRT) of...
1.83 days, influent N-NH$_4^+$/N-NO$_3^-$ ~ 1), the ammonia removal steadily increased to ~ 40% (Figure 1a) while nitrate removal was higher than 90% with generally low concentrations of nitrate and nitrite in the effluent (Figure 1b). It should be noted that, throughout the entire period of study, the effluent concentrations of VFA were at or below the detection limit of FID-chromatography used (10 mg COD/l) and the effluent COD values were around 20–25 mg/l. Also, due to consumption of VFA and generation of bicarbonate alkalinity (reactions 1a and 1b), the effluent pH was around 8.3 in spite of slightly acidic influent fed (section 2.1) during all the experiments with synthetic wastewater. As a result of development of full denitrification and partial ammonia oxidation (Figure 1), the total nitrogen removal also steadily increased to 67% by the end of start-up period (Figure 1a). Since these nitrogen removals were comparable with those for the start-up period of sulphide driven DEAMOX (Kalyuzhnyi et al. 2006), we concluded that the start-up period was successfully completed.

Quasi steady-state performance of the DEAMOX reactor with synthetic wastewater

Since a true steady state is practically impossible to reach for reactors with high sludge retention times (as in our case), quasi steady-state conditions were assumed (and the collection of data started) after at least 5 reactor volumes of feed had passed through the DEAMOX reactor after each change of operational regime.

Variation of NLR. From Figure 2a, it is seen that a decrease of HRT from 1.73 to 0.31 days (and, hence, an increase of NLR from 211 to 1236 mg N/l/d) had almost no influence on the ammonia removal (variation 38–42%); however, it led to a decrease of NO$_x$ removal from 96 to 74%. Both nitrite and nitrate were present in the effluent at average concentrations around 10 and 20 mg N/l, respectively (data not shown). As a result, the average total N removal also decreased from 66 to 56%. The most noticeable deterioration of the process performance occurred under the shortest HRT of 0.31 days when the concentration of nitrate increased to 40 mg N/l (data not shown). The average ratio of ammonia consumed versus nitrate consumed was pretty stable, around 0.5 (Figure 2b), indicating a noticeable ammonia oxidation according to reaction 2 but also about a significant occurrence of unwanted reaction 1b (otherwise this ratio should be close to 1). The average ratio of COD consumed/N-NO$_3^-$ consumed had a tendency to increase (from 2.65 to 2.98, Figure 2b) with decreasing HRT and was substantially higher than the theoretical value for partial denitrification of nitrate to nitrite (1.9), showing that there was a substantial COD expense for undesired nitrite denitratation (reaction 1b). The effluent contained only traces of acetate in these and subsequent experiments.

Variation of COD source. From Figure 3, it is seen that acetate alone seems to be slightly less suitable as a substrate for full denitrification compared to VFA mixture (Figure 3b) because the efficiency of nitrate removal dropped (it was present at concentrations around 40 mg N/l, data not shown), however, the efficiency of ammonia removal was comparable (Figure 3a). As a result, the overall efficiency of nitrogen removal slightly dropped in the case of acetate (Figure 3a). Taking into account all these observations
(especially, no deterioration of ammonia removal), the further experiments were conducted with only acetate as a COD source for partial denitrification.

**Variation of influent COD/N-NO₃² ratio.** It is seen (Figure 4a) that the increase of this ratio from 1.90 to 3.48 led to a substantial enhancement of average ammonia removal (from 32 to 53%) and almost complete NOₓ species removal (increase from 59 to 99%). As a result, the average total N removal also increased from 46 to 77% (Figure 4a). The most significant deterioration of the process performance occurred under the smallest influent COD/N-NO₃² ratio of 1.90 due to a shortage of COD donor for denitrification of nitrate to nitrite; effluent nitrate concentrations were as high as 70–80 mg N/l (data not shown). The average ratio of ammonia consumed/nitrate consumed had a slight decreasing trend (from 0.54 to 0.52) whereas the average ratio of COD consumed/N-NO₃² consumed had a slight tendency to increase (from 3.22 to 3.45) with increasing influent COD/N-NO₃² ratio (data not shown). In fact, under the highest influent COD/N-NO₃² ratio applied, practically only ammonia (with traces of nitrite and nitrate) was present in the effluents. The further increase of influent COD/N-NO₃² ratio above 3.48 did not enhance the process performance and in some instances even led to its slight deterioration (data not shown) due to an excessive occurrence of reaction 1b.

**Variation of influent NH₄⁺/N-NO₃² ratio.** It is seen (Figure 4b) that the decrease of this ratio from 1 to 0.29 led to a substantial increase of average ammonia removal (from 53 to 80%) resulting in the increase of average total N removal.
from 71 to 95% (removal of NOx species was almost complete). The average ratio of ammonia consumed/nitrate consumed decreased (as expected) from 0.52 to 0.24 whereas the average ratio of COD consumed/N-NO3 consumed had a slight tendency to increase (from 3.45 to 3.57) with decreasing influent N-NH4+/N-NO3 ratio (data not shown).

Treatment of real reject water

Taking into account the auxiliary role of the nitrifying reactor (nitrate generation for the DEAMOX reactor) in our study and the 100% nitrification efficiency usually observed, its performance will not be discussed here. Since the composition of the mixture of raw reject water and nitrified effluent (~50:50) was similar to that of synthetic wastewater used earlier, no noticeable deterioration of process performance of the DEAMOX reactor was observed even in the first few days after beginning treatment of this substrate (data not shown).

Variation of NLR. From Figure 5a, it is seen that a decrease of HRT from 0.96 to 0.32 days (and, hence, an increase of NLR from 361 to 1243 mg N/l/d) led to a decrease of average ammonia removal from 47 to 40%, whereas the average NOx removal was always higher than 93%. Both nitrite and nitrate were present (except in the last run) in the effluents at concentrations 1–10 mg N/l (data not shown). As a result, the average total N removal also slightly decreased from 71 to 66% with decreasing HRT (Figure 5a). Some deterioration of the DEAMOX reactor performance under the shortest HRT applied was also due to a decrease of ammonia conversion (to 90%) in the preceding nitrifying reactor. This led to some deficiency of NOx species in the DEAMOX reactor (they were completely absent in the
effluent) and some surplus of ammonia thus creating stoichiometric limitations for reaction 2. The average ratio of ammonia consumed versus nitrate consumed was around 0.5 during the first 3 runs but then increased to 0.58 under the highest NLR applied (Figure 5b). It seems that nitrate deficiency enhances (to some extent) nitrite utilisation by anammox reaction 2 over competing reaction 1b. The average ratio of COD consumed/N-NO₃ consumed had a slight tendency to increase (from 3.32 to 3.48, Figure 5b) with increasing NLR. The effluent contained around 300 mg COD/l which was presumably non-biodegradable under the DEAMOX conditions.

CONCLUSIONS

The study with synthetic wastewater showed a principal feasibility of the DEAMOX process under replacement of sulphide by VFA as an electron donor for production of nitrite. However, VFA were less efficient (in terms of COD required) for this purpose because it was difficult to prevent an occurrence of reaction 1b.

The testing of the VFA driven DEAMOX process with real reject water showed that a stable process performance up to NLRs of 1243 mg N/l/d (in the DEAMOX reactor) is achievable with 40, ~100, and 66% of ammonia, NO₃⁻ and total nitrogen removals, respectively. Though around 30% of initial ammonia is left in the DEAMOX effluents which should be further treated in the main WWTP, the developed process offers substantial savings for treatment of strong nitrogenous anaerobic effluents compared to conventional nitrification-denitrification.

REFERENCES

