HIGH-RATE DENITRIFICATION OF CONCENTRATED NITRATE WASTEWATER

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ABSTRACT

The principles of high-rate denitrification are explained. In the experimental section of the paper the results of nine lab-scale experiments are described and compared with data gained from reviewed literature. The tests were performed in continuous flow stirred-tank and wash-out reactors under mesophilic and thermophilic conditions. The experimental results confirm that high-rate denitrification is an extremely efficient process. Removal rates of up to 25 kg NO₃-Nel./(m³·d) were achieved with the activated sludge systems.

The nitrate sludge loading was found to be the significant design parameter for the process if there is an excess of organic substrate. The maximum rate achieved by thermophilic bacteria was 10 kg NO₃-Nel./(kg MLVSS·d) which exceeded by 33 % that for mesophilic organisms. Due to this, in the wash-out reactors the thermophilic system was superior to the mesophilic at system-related, inevitably similar MLVSS concentrations. But because of a temperature-dependent type of growth (thermophilic: disperse; mesophilic: flocculating), in the case of systems with recycling of biomass, higher removal rates (per volume) were obtained for the mesophilic reactors.

KEYWORDS

Wastewater treatment, biological denitrification, water pollution control, nitrate, nitrite, nitrate reduction, activated sludge process, wash-out process, mesophiles, thermophiles.

1. INTRODUCTION

The denitrification of high-nitrate wastewater is a major problem for many industries, for example those chemical branches involved in fertilizer or cellophane production, pectin production from apples or citrus peels, or uranium oxide fuel production, just to mention a few.

The experiments described in this article were performed with wastewater generated in the production of pectin, a thickener used in many food products. The production process involved extraction of plant material with nitric acid. The nitrate in the wastewater was accompanied mainly by carbohydrates and a small amount of alcohol. Nitrate concentrations of 1,200 - 1,760 mg NO₃-N/l were encountered along with a COD of 11,200 - 14,900 mg/l. The experiments were de-
signed to test the feasibility of biological denitrification in such wastewater at mesophilic and thermophilic temperatures. Further sought were the conversion coefficients and the parameters influencing the process.

2. BIOLOGICAL DENITRIFICATION

Biological denitrification can be achieved with the help of autotrophic as well as heterotrophic organisms (Claus and Kutzner, 1984). The autotrophic bacteria require elemental sulphur or thiosulphate as an energy source (Alexander, 1981; Mann, 1972). In wastewater treatment, the presence of organic compounds serving as an electron source make heterotrophic denitrification the more common process. Of the 1.5 mol O₂ per mol nitrate-N, 1.25 mol are released for COD removal. That corresponds to an oxygen release of 2.85 g/g relative to nitrogen. At the same time, one mol alkali per mol denitrified N is produced. This means that 71 mVal alkali per 1 g nitrogen are produced in denitrification. As shown in Fig. 1, denitrification occurs in four steps.

From a processing standpoint, the intermediate product nitrite is of some importance because it can occasionally reach considerable concentrations in the reactor (Claus and Kutzner, 1984). In a simplified scheme, the reactions involving the intermediate nitrite are:

\[
\begin{align*}
\text{Eq. 1} & \quad \text{NO}_3^- + 2 \text{H}^+ \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \\
\text{Eq. 2} & \quad \text{NO}_2^- + 3 \text{H}^+ + \text{H}^+ \rightarrow 0.5 \text{N}_2(g) + 2 \text{H}_2\text{O}
\end{align*}
\]

The amount of oxygen released per gram of nitrogen and being available for COD removal is 1.14 g O₂ in Eq.1 and 1.71 g O₂ in Eq.2. The amount of carbon stoichiometrically required in denitrification is given in Eq.3, whereby methanol represents the carbon source and carbon incorporated into cell material is disregarded.

\[
\text{Eq. 3} \quad 5 \text{CH}_3\text{OH} + 6 \text{NO}_3^- \rightarrow 5 \text{CO}_2 + 3 \text{N}_2 + 7 \text{H}_2\text{O} + 6 \text{OH}^-
\]

The amount of methanol required for denitrification is thus 1.9 per gram nitrogen, corresponding to a COD of 2.85 g.

3. DATA FROM THE LITERATURE

A literature review published in 1975 by Francis and Callahan provided the following data concerning high-rate denitrification:
- The pH range favorable for denitrification is between 7.5 and 8.5.
- The process converting nitrate to nitrite is less sensitive to drops in pH than that converting nitrite to nitrogen gas.
- Reports concerning the influence of temperature on the process are contradictory. Whereas in one contribution (Stensel et al., 1973) no change was observed upon increasing temperature from 20 °C to 30 °C, other authors (Cooper and Smith, 1983; Mechalas et al., 1970) detected the typical twofold increase in reaction rate for 10 °C increase in temperature between 15 °C and 30 °C. The temperature optimum was found to be 60 °C.
- It is suspected that poorly degradable carbon sources result in nitrate-ammonification instead of nitrate-denitrification.
- The conversion of nitrate proceeds with a maximum rate at NO₃-N concentrations down to almost 1 mg/l. The Michaelis constant \(k_m\) is between 0.06 and 0.08 mg NO₃-N/l. With organic substrate as the limiting factor, a \(k_m\) of 5.8 mM was found using sodium acetate.
- The specific excess sludge production, \(E_{SP}\), was given as 0.18 kg MLVSS/kg CODel.

The literature search revealed widely varying denitrification rates. Values were...
for the volumetric removal rate $L'_{V,NOx-N}$ between 0.003 and 1.271 kg NO$_3$-N/(m$^3$·d) and for the removal rate $L'_{MLSS,NOx-N}$ between 0.012 and 0.324 kg NO$_3$-N/(kg MLSS·d).

Mudrak (1970) conducted extensive laboratory, semitechnical and full scale tests on denitrification in wastewater from a cellulose-processing chemical plant. As in pectin waste, the nitrate resulted from the use of nitric acid. It should be noted, however, that in contrast to the treatment of pectin waste, the carbon source in the cellulose waste was the limiting substrate. Carbon removal was the primary target of treatment. Nonetheless, several results relevant to the experiments described here were reported:

- The denitrification rate dropped significantly at pH <7 (Mudrak and Hellwig, 1969, p. 366).
- The BOD$_5$-utilization necessary for the denitrification of one gram NO$_x$-N in full scale tests at a sludge loading of $L_{MLSS,BOD5} = 0.3$ BOD$_5$/ (kg MLSS·d) averaged 2.3 g/g (Mudrack, 1970, p. 41).
- At volumetric loadings of $L_{V,BOD5} = 2.3$ kg BOD$_5$/ (m$^3$·d) and influent concentrations of $C_{0,NO3-N} = 250$ mg/l, effluent concentrations of approx. 50 mg/l NO$_2$-N were observed.
- At an average sludge loading of $L_{MLSS,BOD5} = 0.3$ kg BOD$_5$/ (kg MLSS·d), the excess sludge production was $E_S^{sp} = 0.34$ kg MLSS/kg BSB$5_{el}$ (Mudrack, 1970).

The denitrification experiments of Haltrich (1968) were performed at relatively low influent concentrations of 80-120 mg NO$_3$-N/l. He reached the following conclusions:

- As long as the ratio of BOD$_5$ influent concentration to NO$_3$-O$_2$ influent concentration was greater than 1.5, complete denitrification occurred. This corresponds to a ratio of $C_{0,BOD5}/C_{0,NO3-N} = 5.1$.
- The maximum nitrogen-sludge-loading at which complete denitrification still occurred was found to be $L_{MLVSS} = 0.44$ kg NO$_3$-N (kg MLVSS·d).
- The specific BOD$_5$ utilization per gram nitrate removed increased from 3.4 g/g (at $C_{0,BOD5}/C_{0,NO3-N} = 3.4$) to 6.2 g/g (at $C_{0,BOD5}/C_{0,NO3-N} = 24$) (p. 160); i.e., the amount of carbon removed per unit of nitrate increased with increasing abundance of organic substrate (see Fig. 6).

### 4. MATERIALS AND METHODS

Experiments were performed on a laboratory scale. Five units were available which could either be operated with clarifier as activated sludge plants or without clarifier as wash-out reactors. Operated as an activated sludge process, no deliberate wasting of sludge was carried out. The excess sludge left the systems continuously via the effluent of the clarifiers. Technical data for the individual systems are given in Tab. 1. The flow sheet for the units is shown in Fig. 2.

<table>
<thead>
<tr>
<th>TABLE 1 Technical data of the experimental plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactor type</td>
</tr>
<tr>
<td>number of units</td>
</tr>
<tr>
<td>inner diameter (cm)</td>
</tr>
<tr>
<td>volume (l)</td>
</tr>
<tr>
<td>heating system</td>
</tr>
</tbody>
</table>

For the start-up, sludge from the anaerobic reactor of a technical scale pectin wastewater treatment plant was used as inoculum. To insure an adequate supply of phosphorus, phosphoric acid was added to the waste in all tests. The duration of each test and the chronological order are given in Fig. 3. For each test the number, reactor type and operating temperature are shown. Further parameters are given in Tab. 2.
5. RESULTS

Since denitrification did not always proceed to the $N_2$ level, considerable concentrations of $NO_2^-$ in the effluent were sometimes encountered. Therefore, effluent concentration and removal efficiency are given in terms of $NO_x-N$. As a result, values determined for removal efficiency disregard any conversion of nitrate to nitrite.

5.1 ACTIVATED SLUDGE REACTORS

Test 1 (ASR, 55 °C) was designed to provide some initial data concerning denitrification in the thermophilic range. The detention time at start-up was 3.8
### TABLE 2 Experimental parameters and results

<table>
<thead>
<tr>
<th>test number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of reactor, temperature (°C)</td>
<td>ASR,55</td>
<td>ASR,55</td>
<td>ASR,55</td>
<td>T</td>
<td>ASR,32</td>
<td>ASR,41</td>
<td>ASR,52</td>
<td>ASR,61</td>
<td>WOR,32</td>
<td>WOR,41</td>
</tr>
<tr>
<td>test condition</td>
<td>( \text{d)} t_R )</td>
<td>( \text{d)} t_R )</td>
<td>( \text{l} T )</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>( \text{d)} t_R )</td>
<td>( \text{d)} t_R )</td>
</tr>
<tr>
<td>( t_R ) (h)</td>
<td>8.0-2.0</td>
<td>10.0-3.0</td>
<td>3.0</td>
<td>2.0</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.0</td>
<td>15.0-0.5</td>
<td>15.0-0.5</td>
</tr>
<tr>
<td>( T ) (°C)</td>
<td>55</td>
<td>55</td>
<td>58-83</td>
<td>32</td>
<td>41</td>
<td>52</td>
<td>61</td>
<td>32</td>
<td>41</td>
<td>62</td>
</tr>
<tr>
<td>redox potential ( E_h ) (mV)</td>
<td>( &lt;-230 )</td>
<td>( &lt;171 )</td>
<td>( &gt;-251 )</td>
<td>( &gt;-94 )</td>
<td>( &lt;-24 )</td>
<td>( &gt;-170 )</td>
<td>( &gt;-260 )</td>
<td>( &gt;-278 )</td>
<td>( &gt;-225 )</td>
<td></td>
</tr>
<tr>
<td>( C_{o,COD} ) (mg/l)</td>
<td>11,200</td>
<td>12,740</td>
<td>12,970</td>
<td>13,700</td>
<td>13,700</td>
<td>13,700</td>
<td>13,700</td>
<td>11,470</td>
<td>12,100</td>
<td>12,100</td>
</tr>
<tr>
<td>( C_{e,COD} ) (mg/l)</td>
<td>6,700</td>
<td>6,780</td>
<td>5,800-9,800</td>
<td>5,160</td>
<td>5,950</td>
<td>6,780</td>
<td>7,730</td>
<td>6,581</td>
<td>15,410-12,510</td>
<td>16,790</td>
</tr>
<tr>
<td>( C_{o,NO_3-N} ) (mg/l)</td>
<td>1,200</td>
<td>1,210</td>
<td>1,250</td>
<td>1,220</td>
<td>1,220</td>
<td>1,220</td>
<td>1,340</td>
<td>1,450-1,760</td>
<td>1,450-1,760</td>
<td>1,450-1,760</td>
</tr>
<tr>
<td>( C_{e,NO_3-N} ) (mg/l)</td>
<td>-</td>
<td>-</td>
<td>0-1,000</td>
<td>-</td>
<td>-</td>
<td>3) 217</td>
<td>3) 203</td>
<td>3) 150-780</td>
<td>3) 0-1,470</td>
<td>3) 0-1,400</td>
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<tr>
<td>( C_{e,NH_4-N} ) (mg/l)</td>
<td>10</td>
<td>270</td>
<td>47-120</td>
<td>8.5</td>
<td>19.5</td>
<td>66.4</td>
<td>80-800</td>
<td>35</td>
<td>675-62</td>
<td>260-36</td>
</tr>
<tr>
<td>( C_{e,CH_3COOH} ) (mg/l)</td>
<td>340</td>
<td>438</td>
<td>475</td>
<td>475</td>
<td>475</td>
<td>475</td>
<td>475</td>
<td>420</td>
<td>435</td>
<td>435</td>
</tr>
<tr>
<td>( C_{e,CH_3COOH} ) (mg/l)</td>
<td>2,050</td>
<td>2,075</td>
<td>2,153</td>
<td>2,172</td>
<td>2,172</td>
<td>2,172</td>
<td>2,172</td>
<td>1,542</td>
<td>180-2,200</td>
<td>283-2,140</td>
</tr>
<tr>
<td>( C_{COD-el} ) (mg/l)</td>
<td>( (-) )</td>
<td>( 3.8 )</td>
<td>( 4.9 )</td>
<td>( 3.6-14.2 )</td>
<td>( 7.0 )</td>
<td>( 6.4 )</td>
<td>( 6.9 )</td>
<td>( 5.9 )</td>
<td>( 4.8 )</td>
<td>( 4.6-8.2 )</td>
</tr>
<tr>
<td>( C_{NO_2-N,el} ) (mg/l)</td>
<td>( 14.4 )</td>
<td>( 8.12 )</td>
<td>( 9.64 )</td>
<td>( 14.7 )</td>
<td>( 14.1 )</td>
<td>( 14.0 )</td>
<td>( 14.0 )</td>
<td>( 16.0 )</td>
<td>( 2.7-84.8 )</td>
<td>( 23-84.5 )</td>
</tr>
<tr>
<td>( L^{'}_{V,NO_2-N} ) (kg NO_2-N/m³-d)</td>
<td>( 14.4 )</td>
<td>( 8.12 )</td>
<td>( 3) 0.3-5.9 )</td>
<td>( 14.7 )</td>
<td>( 14.1 )</td>
<td>( 3) 11.5 )</td>
<td>( 3) 11.7 )</td>
<td>( 12.3 )</td>
<td>( max.: 14.0 )</td>
<td>( max.: 18.5 )</td>
</tr>
<tr>
<td>( L^{'}_{V,NO_3-N} ) (kg NO_3-N/m³-d)</td>
<td>( 154 )</td>
<td>( 40 )</td>
<td>( 103 )</td>
<td>( 90 )</td>
<td>( 79 )</td>
<td>( 69 )</td>
<td>( 59 )</td>
<td>( max.: 76 )</td>
<td>( max.: 73 )</td>
<td></td>
</tr>
<tr>
<td>( L^{'}_{MLVSS,NO_2-N} ) (kg NO_2-N/kg MLVSS)</td>
<td>( 1) )</td>
<td>( 1.2 )</td>
<td>( 4.23 )</td>
<td>( 0.56 )</td>
<td>( 0.75 )</td>
<td>( 3.22 )</td>
<td>( 11.28 )</td>
<td>( 4) )</td>
<td>( 0.7 )</td>
<td>( 58.9 )</td>
</tr>
<tr>
<td>( L^{'}_{MLVSS,NO_3-N} ) (kg NO_3-N/kg MLVSS)</td>
<td>( 1) )</td>
<td>( 1.2 )</td>
<td>( 4.23 )</td>
<td>( 0.56 )</td>
<td>( 0.75 )</td>
<td>( 2.65 )</td>
<td>( 3) 4) 4.49 )</td>
<td>( 11.2 )</td>
<td>( max.: 7.5 )</td>
<td>( max.: 10.0 )</td>
</tr>
<tr>
<td>( M L V S S_p f ) (g/l)</td>
<td>( 2) 18 )</td>
<td>( 5) 2.3 )</td>
<td>( 1.7-10.2 )</td>
<td>( 28.9 )</td>
<td>( 22.9 )</td>
<td>( 7.7 )</td>
<td>( 4.9 )</td>
<td>( 4) )</td>
<td>( 1.6-3.6 )</td>
<td>( 4) )</td>
</tr>
<tr>
<td>( M L V S S_p f ) (g/l)</td>
<td>( 12 )</td>
<td>( 5) 1.7 )</td>
<td>( 1.3-5.7 )</td>
<td>( 24.6 )</td>
<td>( 18.9 )</td>
<td>( 5.2 )</td>
<td>( 2.9 )</td>
<td>( 1.1 )</td>
<td>( d) )</td>
<td>( 5.4-1) )</td>
</tr>
<tr>
<td>SVI (ml/g)</td>
<td>( 1) )</td>
<td>( 30 )</td>
<td>( 2) 58 )</td>
<td>( 21 )</td>
<td>( 22 )</td>
<td>( 2) 250 )</td>
<td>( 2) 250 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**c)** constant conditions; **1)** increasing; **d)** decreasing; **1)** = at \( t_R = 2 \) h; **2)** = sometimes not determinable; **3)** = in case of concentration: NO₂-N is considered as well as NO₃-N; in case of removal efficiency: conversion from NO₃-N to NO₂-N is disregarded; **4)** = membrane filtration; **5)** = strong foaming.

Days and was reduced over the 11 week test period to 2 hours. During the course of operation, it became evident that recycling of floating sludge from the clarifier was necessary to establish adequate biomass in the reactor. Even at 100% denitrification in the reactor, degassing processes took place in the clarifier causing sludge to float and spill over into the effluent. Therefore an additional device (as shown in Fig. 2) was installed which prevented the rising sludge from being carried out of the system. The results from the last four weeks of operation in test 1 demonstrate a remarkably high efficiency for the denitrifi-
cation process. At test termination, with \( t_R = 2.0 \text{ h} \), a volumetric nitrate removal rate of \( L'V,NO_3-N = 14.4 \text{ kg NO}_3-N/(m^3 \cdot d) \) and a simultaneous COD elimination of \( L'V,COD = 54 \text{ kg COD/(m}^3 \cdot d) \) were observed. Denitrification was complete.

The test plant was expanded by the addition of type II reactors. Test 2 (ASR, 55 °C) was initiated early to provide inoculum for tests 4-7 (see Fig. 3). The results of test 2 confirmed the results of test 1 with the exception of the following two points:
- despite identical external experimental parameters, the MLSS concentration could not be brought back up to the same high level of 18 g/l
- despite the same NH\(_4\)-N influent concentration (approx. 70 mg/l), a certain amount of ammonification occurred in test 2. The average NH\(_4\)-N-effluent concentration was 270 mg/l. The low MLSS-concentrations were due to an intense foam production which allowed biomass to escape from the reactor.

In test 3 the reactor temperature was gradually increased to determine the maximum temperature at which denitrification still occurs. The detention time was chosen to be 3 hours (\( L'V,NO_3-N = 9.6 \text{ kg NO}_3-N/(m^3 \cdot d) \)). The curve in Fig. 4 contains the following information:
- Up to a temperature of 62 °C, denitrification proceeded to completion.
- Between 62 °C and 72 °C a slight drop of efficiency occurred which became more pronounced at temperatures above 72 °C. At just under 80 °C, denitrification efficiency was only \( n_{NO_3-N} = 50 \% \).
- At 83 °C, the production of nitrogen gas ceased entirely; still little reduction to nitrate occurred.
- Whenever denitrification was incomplete, NO\(_2\) could be detected. The absolute NO\(_2\)-N concentration increased only slightly with increasing temperature.

Tests 4-7 were run for 50 to 60 days under constant external conditions at different temperatures in order to clarify more precisely matters concerning the effect of operating temperature upon the denitrification process at steady state. The systems were operated under high loading at a detention time of 2 hours. The resulting volumetric loadings were (see also Tab. 2):
\[
L'V,NO_3-N \approx 14 \text{ kg NO}_3-N/(m^3 \cdot d) \\
L'V,COD \approx 164 \text{ kg COD/(m}^3 \cdot d) .
\]

It was found that the sludge in the two mesophilic systems (test 4, \( T = 32 \text{ °C} \); test 5, \( T = 41 \text{ °C} \)) tended towards floc-forming growth, whereas in the thermophilic systems (test 6, \( T = 52 \text{ °C} \); test 7, \( T = 62 \text{ °C} \)) a disperse growth of single cells was seen. This was monitored by microscopic analysis and additionally observed as increased turbidity in the reactor contents. Such sludge therefore displayed poor settling and thickening properties. Since no deliberate measures were taken to remove excess sludge, equilibrium MLSS concentrations in the reactors were determined solely by the thickening properties of the return sludge. All of the systems had return sludge ratios of 200 \%. In Fig. 5, the equilibrium MLSS-concentrations are shown as a function of operating temperature. The ther-

Fig. 4. Influence of increasing operating temperature upon NO\(_X\)-N concentration

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mophilic systems had significantly lower MLSS concentrations than the mesophilic systems. At the same time, the portion of volatile solids also decreased. It should, however, be noted that the measurement of MLSS concentrations was performed by the standard paper filtration method in which disperse single bacterial cells are not detected. Membrane filtrations of the paper filtrates revealed an additional 2.0 g MLSS/l of high organic content. The excellent settling properties of the mesophilic sludge were evidenced by a sludge index of slightly over 20 ml/g. At higher temperatures, the sludge index was no longer a valid indicator since phase boundaries between sludge and water were sometimes difficult to discern. Whereas denitrification was complete in the mesophilic systems, the thermophilic systems showed some instability due to the low concentration of bacteria. The average NO₃-N effluent concentrations in the thermophilic systems were just above 200 mg/l, whereby the NO₂ component was sometimes up to 90% of the NO₃-N concentration. The highest volumetric removal rate was achieved in test 4 (ASR, 32 °C), the values obtained being:

\[
\begin{align*}
L'V,N_{\text{NO}_3-N} & = 14.7 \text{ kg NO}_3-N/\text{m}^3\cdot\text{d} \\
\eta_{\text{NO}_3-N} & = 100 \text{ %,} \\
L'V,COD & = 103 \text{ kg COD}_{\text{el.}}/\text{m}^3\cdot\text{d}.
\end{align*}
\]

Fig. 5. MLSS concentration of the reactor as a function of operating temperature in four different systems (excess sludge leaving systems via effluent)

COD removal relative to NO₃-N consumption in all four systems was fairly high in comparison to the results of the other tests shown in Tab. 2. The system operating at T = 32 °C yielded an average value of 7.00 g/g, higher than 5.87 g/g found in the system run at T = 61 °C. Whereas the NH₄-N effluent concentrations in the thermophilic systems were found to remove NH₄-N to residual effluent concentrations of under 20 mg/l. Nitrate ammonification was not observed in any case.

Fig. 6 shows the dependence of the ratio of COD removed to NO₃-N removed upon the ratio of COD to NO₃-N in the influent. The amount of COD removed per unit nitrogen removed clearly increases with an increase in the corresponding influent ratio. Besides the averages from tests 5 and 7 the graph contains results from two tests not listed in Tab. 2. In these two experiments the nitrate concentration of the influent was increased while the COD concentration was kept constant. The mesophilic systems were capable of eliminating more carbon per utilized unit of nitrate-oxygen than their thermophilic counterparts. The values of Haltrich (1968), also shown in Fig. 6, are very similar to our own, although the concentrations in his experiments were considerably lower. The volumetric loading of BOD₅ was also high, with values ranging from 3 to 43 kg BOD₅/ (m³⋅d) and BOD₅ sludge loading spanning from 0.6 to 4.4 kg BOD₅/(kg MLVSS⋅d).

The rate of microbial conversion processes is determined by the number of bacteria and their maximal growth rate. Out-wash experiments, in which sludge is not recycled, are suited to find these parameters which are significant for the process. Therefore, subsequently to test 4, the clarifier was disconnected and test 8 (T = 32 °C) was performed (see Fig. 3). The denitrification efficiency dropped from \( \eta_{\text{NO}_3-N} = 100 \text{ %} \) (with recycling of biomass) to levels between 42% and 89% at a detention time of 2 hours and with a volumetric loading of \( L'V,\text{NO}_3-N = 16 \text{ kg NO}_3-N/\text{m}^3\cdot\text{d} \). The MLSS concentration in the reactor stabilized at a level of about MLSS = 3.0 g/l.

5.2 WASH-OUT REACTORS

The results from test 8 prompted two further experiments with wash-out reactors, tests 9 and 10. Test 9 was performed at T = 41 °C for 20 days, test 10 at T = 62 °C for 24 days. Since both reactors were previously operated as activated sludge
systems, the clarifiers only had to be disconnected. Detention times were initially extended to 15 hours and gradually reduced during the course of the tests to 0.5 hours. All other external factors were held constant (see Tab. 2). The results of these two tests are given in Figs. 7-10. Fig. 7 and 8 depict the nitrogen removal efficiency and the volumetric nitrogen removal rate in relation to the volumetric loading, whereas in Fig. 9 and 10 the removal data are shown in relation to the sludge loading. The MLVSS concentrations used to evaluate the sludge related values were determined by the membrane filter method (\( \phi = 0.45 \mu m \)).

Due to a drop in pH and an accumulation of nitrite, measurements obtained in the thermophilic reactors at a detention time of \( T_R = 1.0 \) h were discarded since the removal process had collapsed. The system recovered after adjusting the pH to 7.5, and the detention time was simultaneously reduced to 0.5 hours. This occurrence generally indicates that thermophilic systems are more difficult to regulate and more susceptible to pH variation than their mesophilic counterparts.

The maximum denitrification efficiencies shown in Figs. 7-10 correlate to the removal efficiencies given in Tab. 3.

TABLE 3 Removal efficiencies NO\(_x\)-N at maximum denitrification rates in tests with wash-out reactors

<table>
<thead>
<tr>
<th></th>
<th>mesophilic</th>
<th>thermophilic</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \max L' )</td>
<td>( V_{\max} ) NO(_x)-N</td>
<td>( V_{\max} ) MLVSS, NO(_x)-N</td>
</tr>
<tr>
<td>( \frac{\text{mg NOx-N}}{\text{m}^3 \cdot \text{d}} )</td>
<td>( \frac{\text{mg NOx-N}}{\text{g MLVSS} \cdot \text{d}} )</td>
<td>( \frac{\text{mg NOx-N}}{\text{g MLVSS} \cdot \text{d}} )</td>
</tr>
<tr>
<td>( T = 41 \degree C )</td>
<td>13.9</td>
<td>18.6</td>
</tr>
<tr>
<td>( T = 62 \degree C )</td>
<td>7.5</td>
<td>10.0</td>
</tr>
<tr>
<td>removal efficiency</td>
<td>( \eta_{\text{NOx-N}} ) %</td>
<td>( \eta_{\text{NOx-N}} ) %</td>
</tr>
<tr>
<td>(at ( \max ) removal rate)</td>
<td>( \Rightarrow 38 )</td>
<td>( \Rightarrow 55 )</td>
</tr>
<tr>
<td>( \eta_{\text{NOx-N}} ) %</td>
<td>( \Rightarrow 26 )</td>
<td>( \Rightarrow 31 )</td>
</tr>
</tbody>
</table>

In operation as wash-out reactors, thermophilic systems performance was superior to mesophilic systems, the former, however, representing a more delicate process. For a given loading, higher removal efficiencies were obtained in the thermophilic system. For example, at a detention time of two hours, the thermophilic system reached a removal efficiency of \( \eta_{\text{NOx-N}} = 78 \% \) as compared to \( \eta_{\text{NOx-N}} = 56 \% \) for the mesophilic reactor. For an influent concentration of \( C_\text{in,NOx-N} = 1,750 \) mg/l, these translate into effluent concentrations of \( C_\text{out,NOx-N} = 385 \) mg/l and \( 770 \) mg/l, respectively. The maximum thermophilic removal rates were about 33 % higher than those for the mesophilic system, and the maximum loading, at which complete denitrification still occurred, was also significantly higher in the thermophilic system (Figs. 7-10).

The operation as wash-out reactor provides good conditions for determining the specific excess sludge production \( E_{\text{SSP}} \). Thirty measurements were made for each
Fig. 7. Response of removal efficiency $\eta_{\text{NO}_x-N}$ and volumetric removal rate $L'v_{\text{NO}_x-N}$ to increasing volumetric loadings (through decreased detention times) in a mesophilic wash-out reactor (test 9, 41 °C).

Fig. 8. Response of removal efficiency $\eta_{\text{NO}_x-N}$ and volumetric removal rate $L'v_{\text{NO}_x-N}$ to increasing volumetric loadings (through decreased detention times) in a thermophilic wash-out reactor (test 10, 62 °C).

The results shown in Tab. 4 are based on a BOD5/COD ratio of 0.65 in the influent and volatile portions of the sludge of 82% for the mesophilic and 77% for the thermophilic system. All thirty measurements were taken at volumetric loadings (range: 12.5 kg BOD5/(m³·d) to 375 kg BOD5/(m³·d)) higher than those of the usual aerobic activated sludge process. A correlation between volumetric loading and sludge production could not be established. Despite the high volumetric loading, excess sludge production remained under 1.0 kg MLSS/kg BOD5, el., a com-
Response of removal efficiency $\eta_{\text{NOx-N}}$ and removal rate $L'_{\text{MLVSS,NOx-N}}$ to increasing sludge loadings (through decreased detention times) in a mesophilic wash-out reactor (test 9, 41 °C).

Response of removal efficiency $\eta_{\text{NOx-N}}$ and removal rate $L'_{\text{MLVSS,NOx-N}}$ to increasing sludge loadings (through decreased detention times) in a thermophilic wash-out reactor (test 10, 62 °C).

Comparatively low level relative to the aerobic activated sludge process. In lower loading ranges, Mudrack (1970) also found values significantly lower than those of the aerobic activated sludge process (see "data from the literature").

### TABLE 4 Specific excess sludge production $\text{ES}_{\text{sp}}$ in wash-out reactors

<table>
<thead>
<tr>
<th>Specific excess sludge production $\text{ES}_{\text{sp}}$</th>
<th>Mesophilic, $41 \degree \text{C}$</th>
<th>Thermophilic, $62 \degree \text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg MLVSS</td>
<td>0.49</td>
<td>0.42</td>
</tr>
<tr>
<td>kg COD$_{\text{el.}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>kg MLSS</td>
<td>0.60</td>
<td>0.55</td>
</tr>
<tr>
<td>kg COD$_{\text{el.}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>kg MLVSS</td>
<td>0.75</td>
<td>0.65</td>
</tr>
<tr>
<td>kg BOD$_{\text{5,el.}}$</td>
<td>0.92</td>
<td>0.84</td>
</tr>
<tr>
<td>kg MLSS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>kg BOD$_{\text{5,el.}}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. SUMMARY AND CONCLUSIONS

The results show that the high-rate denitrification process is extremely effective. With activated sludge reactors, volumetric removal rates of up to \( L'V, NO_\text{f} = 25 \text{ kg NO}_\text{f}/(\text{m}^3 \cdot \text{d}) \) were achieved, a figure far greater than any other comparable literature value found.

The paramount design parameter for high-rate denitrification with excess organic substrate is the nitrate sludge loading. Removal rates can be predicted from the diagrams in Figs. 9 and 10. The maximum removal rate obtained with thermophilic bacteria was \( L'MLVSS NO_\text{f} = 10 \text{ kg NO}_\text{f}/(\text{kg MLVSS} \cdot \text{d}) \), 33% greater than that obtained with mesophiles. Per unit carbon removed, thermophilic systems consumed more oxygen and produced less excess sludge than mesophilic systems. Both effects can be ascribed to a higher endogenous respiration at the higher temperature range. Because of different sludge properties, however, mesophilic systems are superior to thermophilic systems in cases where biomass is recycled. Much higher MLVSS concentrations are obtained with mesophiles. This cannot be compensated for by the faster conversion rate of the thermophiles.

High-rate denitrification processes are characterized by very high conversion rates but, due to short detention times, are somewhat more sensitive to short term fluctuations in the influent than are large volume treatment processes in which the reactor content simply dilutes influent fluctuations. For this reason the operation of high rate processes requires somewhat more attention.

All reactors were negatively influenced by decreases in pH; each drop below pH 7 disturbed the process. This is illustrated by the relationship between removal efficiency \( \eta_{NO_\text{f}} \) and pH in Fig. 11. The disturbances appeared irrespective of temperature.

![Graph](image-url)

**Fig. 11.** Dependence of removal efficiency \( \eta_{NO_\text{f}} \) upon pH in the reactor

**NOMENCLATURE**

- **WOR**: wash-out reactor (continuous-flow stirred-tank reactor without recycle)
- **LV, x**: volumetric loading \( \text{kg/(m}^3 \cdot \text{d}) \)
- **L'V, x**: volumetric removal rate \( \text{kgel.}/(\text{m}^3 \cdot \text{d}) \)
- **ASR**: activated sludge reactor
- **BOD\text{_n}**: biochemical oxygen demand after \( n \) days
LMLSS,x  sludge loading kg/(kg·d)
L'MKSS,x removal rate on the basis of MLSS kgel./(m³·d)
LMLVSS,x sludge loading divided by the organic portion of the kg/(kg·d)
SLVSS sludge (MLVSS)
L'MLVSS,x removal rate on the basis of MLVSS kgel./(m³·d)

C,el. subscript for "removed" (eliminated)
C0,el. effluent concentration mg/l
C0,x influent concentration mg/l
C0,x sub. for concentration of the parameter x mg/l
COD chemical oxygen demand -

VS volatile portion of suspended solids (MLSS/MLVSS)·100 %
SVI sludge volume index ml/g
NOx-N NO₂-N + NO₃-N mg/l
x-Nel. removed NOₓ-N (does not refer to NO₃-N which has only mg/l
been changed into NO₂-N)

CL clarifier -
R reactor m³/d
pf filtered through a paper filter -
T temperature °C
T detention time h, d
TNK total Kjeldahl nitrogen -
MLSS mixed liquor suspended solids mg/l
MLVSS mixed liquor volatile suspended solids mg/l
(= MLSS x (VS/100))
ES excess sludge -
ESsp specific excess sludge production kg MLSS/kgel.
V volume l
x any parameter
ηx removal efficiency concerning parameter x %

REFERENCES