Long term effects of temperature and substrate level on BNR with an external nitrification reactor

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Abstract This study was conducted with a BNR (biological nutrient removal) process with an external nitrification and switching arrangement of anoxic and oxic stages. It was observed that the SPRR (specific phosphorus release rate) and SDNR (specific denitrification rate) were greatly affected by the organic loads, and SDNR had a higher temperature effect than other kinetic rates including nitrification. It was further observed that the stoichiometric values like PHA (poly hydroxyalkanoate) stored for P release and PHA consumed for P uptake also varied. Variations of % Px (phosphorus content) and PHA as intracellular matter suggest the PAOs were more active at lower temperatures with this process configuration, where more than 70% of NH$_4$-N and phosphorus were removed at temperatures below 10°C.

Keywords BNR; denitrification; nitrification; PHA; phosphorus release and uptake; substrate level; temperature

Introduction
There are many papers dealing with the influence of temperature and substrate level on BNR (biological nutrient removal) plants, but there are few papers with actual field conditions. It may be due to the complexity and difficulty of isolating temperature and substrate effects from the operating results. In addition, there could be other factors involved in the nutrient removal efficiencies like treatment schemes, tank configurations and operating skills besides the temperature and substrate level. This study was carried out with a BNR plant operated in actual conditions to measure the effects of temperature and substrate level associated with seasonal weather conditions, which could be characterized by heavy rainfall during summer and low temperature during winter.

It is known that nitrogen removal is significantly affected by temperature, but the effect on PAOs (phosphorus accumulating organisms) is still somewhat in disagreement. The nitrogen manual (U.S. EPA, 1993) and the IWA ASM (Henze et al., 2000) recommend some stoichiometric values and reaction rates for the design of the BNR process. Among them, the reaction rates are varied with temperature, but the stoichiometric values are constant regardless of temperature and the substrate levels. Like the IWA ASM suggests, Brdjanovic et al. (1997) with a lab BPR (biological phosphorus removal) reactor revealed that there are negligible temperature effects on stoichiometric values in COD required for phosphorus release and uptake, but significant effects on kinetic rates in release and uptake. However, Martinez et al. (1991) with a laboratory SBR (sequencing batch reactor) indicated that phosphorus release was more favorable at low temperatures, and COD required for P release was increased proportionally as the temperature increased as Hao et al. (2001) also observed. The nitrification is significantly affected by temperature, but denitrification is more affected by the substrate level (U.S. EPA, 1993). Further, Randall et al. (1992) reported that the temperature effect was more pronounced for nitrifiers than the denitrifiers when comparing the SNR (specific nitrification rate) and SDNR measured in actual plants. The biofilm system has shown less temperature effect.

Storm water reduces sewage concentrations. Henze et al. (1996) indicated that low
loading conditions would reduce the phosphorus release and uptake rates in the BPR process. Termink et al. (1996) and Carucci et al. (1999) experienced that the PHB (polyhydroxybutyrate) depletion with low organic loads reduced BPR efficiencies.

There are four distinctive seasons with an ambient temperature of –15 to +30°C in Korea; rainy and hot during summer, and very cold during winter. Inflow and infiltration during summer significantly reduce the influent concentration. This study was conducted with a BNR process with an external nitrification reactor and switching arrangement of anoxic and oxic stages expecting reduced temperature and substrate effects.

Materials and methods
A pilot plant with 50 m³/d capacity as shown in Figure 1 was operated in actual conditions from April 2000, and this plant was designed to remove both nitrogen and phosphorus. The plant had 100% of both internal sludge recycle and return activated sludge rates. The settled sludge was returned to the anoxic reactor after aeration in the external nitrification reactor. The HRTs based on the influent flow rate were respectively 1 hr for anaerobic, 3 hrs for anoxic (2 stages), 2 hrs for switching reactor, 2 hrs for oxic and 2 hrs external nitrification reactors with 4 hrs for settling. ORP, DO, pH and temperatures were automatically monitored.

During the rainy period, for about 45 days, the switching reactor was operated as an anoxic stage, because the influent was very weak. In addition, the reactor was switched to an aerobic stage when the temperature of the influent declined to less than 17.5°C and the organic load was high enough. The system SRT was controlled from 14.4 to 36.5 days (during the rainy period) with F/M ratios of 0.21 and 0.34 kg COD/kg MLVSS/d.

Soluble items were analyzed daily, and PHA, EPS (extracellular polymeric substances), and phosphate content of biomass (Px) were measured periodically. All analyses were measured in accordance with the Standard methods (APHA et al., 1995). PHA was determined as a sum of PHB and PHV (polyhydroxyvalerate) by the method used by Satoh et al. (1992). EPS was extracted by the method of Zhang (1998), using washing, stripping, extraction, filtration and collection. EPS includes total carbohydrate and protein forms: the former was determined by the procedure of Gerharat et al. (1994), and the latter was measured by the method using bio-rad protein assay kit-2.

Results and discussion
Removal efficiencies with temperature
Raw wastewater could be characterized with an average total COD of about 213.6 mg/L with 20.8% soluble form (Ss), 5.0% VFA form (S_A), and 50.3% slowly degradable form (Xs). The COD, TN and TP loads were respectively 10.84 ± 8.53 kg/d, 1.66 ± 0.65 kg/d and
During the rainy period between day 90 and day 135 in Figure 2, the loads were 4.26 ± 1.59, 1.25 ± 0.37 and 0.11 ± 0.02 kg/d for TCOD, TN and TP, respectively. The COD loads were decreased by 60% of the average loads, while the nutrient loads were decreased by only about 20 to 30%. Consequently, the decreased COD/N and COD/TP ratios were expected to reduce the nutrient removal efficiencies.

Figure 3 shows the nitrogen and phosphorus removal efficiencies. The nitrogen and phosphorus utilized by forming cellular mass were excluded when computing the removal efficiencies. Excellent nitrification was possible with an average of 77%, and more than 70% nitrification was achieved at lower temperatures even below 10°. This was probably due to the external nitrification tank, by which the NH₄-N was reduced to 0.38 mg/L from 1.76 mg/L at this temperature.

Denitrification efficiencies were 45 to 90% with an average of 62%, and it appeared the lower efficiencies were obtained during the lower temperature and rainy periods. TP removal efficiencies ranged from 50 to 95% with an average of 79%, and it appeared the influent characteristic was also important as well as temperature. The lower efficiencies of phosphorus and denitrification still occurred in the rainy period even with the switching reactor being operated as an anoxic stage. In addition, it was noticed that the phosphorus
removal efficiencies were greatly improved from 350 days, while the denitrification efficiencies were reduced. This seemed due to the characteristics of the flow scheme of the proposed process, which was designed to provide more food in favor of PAO competing with denitrifiers.

**Kinetic rates**

Figure 4 shows the specific phosphorus and nitrogen removal rates with temperature and influent COD loads. It was difficult to isolate the temperature effect from the combined effects with variation of COD loads. For this reason, the temperature coefficients as shown in Table 1 were computed at the same organic loads which occurred from days 180 to 355 from Figure 4. The coefficients were computed by using the Arrhenius expression with $\gamma_T = \gamma_{20} \times \theta^{(T-20)}$. Generally, this system seemed to show different temperature effects in comparison to the other systems reported previously. For instance, the temperature coefficient of SNR was only about 1.04, which is rather similar to that of the fixed bed (Canziani et al., 1999), but denitrification showed the highest coefficient of 1.07.

Table 1 also compares the reaction rates at different organic levels which occurred between rainy and dry periods above 20\°C. Generally, the denitrification rates was greatly affected by the substrate level, and the phosphorus release rate, appeared more dependent on substrates than phosphorus uptake, but the nitrification rate was not affected very much by the substrate level.

**Stoichiometric values**

Table 1 also shows the computed stoichiometric values used for BNR design. The COD consumed for P released was smaller at the lower load than at the higher load above 20\°C. The conversion efficiencies from the soluble COD consumed for the PHA stored for P released were 0.15 to 0.8. The PHA stored for P released also varied from 1.1 to 2.3 g COD/g P released, while the PHA consumed for P uptake was 0.22 to 0.65 g CPD/g P; the IWA ASM recommended 2.5 and 0.2 respectively for the values.

The COD consumed/NO₃-N removed varied with SRT, heterotrophic yield ($Y_H$) and endogenous respiration rate. Assuming $Y_H$ equals 0.63 gCOD/gCOD, and the endogenous respiration rate is varied with a temperature coefficient of 1.047, the estimated COD required for NO₃-N removed was compared with the measured, from which it could be noticed there were some differences, but it could be said the heterotrophic yield from denitrification might not be assumed to be constant (see Figure 5).
**Table 1** Summary of kinetic and stoichiometric values

(a) Temperature coefficients and kinetic rates

<table>
<thead>
<tr>
<th>Kinetic rates, (g/kg MLVSS/d)</th>
<th>Temperature Coefficients, (θ)</th>
<th>Specific reaction rates, (g/kg MLVSS/d)</th>
<th>Remarks</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Rainy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRR</td>
<td>1.04</td>
<td>94.0</td>
<td>68.0</td>
<td>1.055–1.096</td>
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<td>SPUR</td>
<td>1.03</td>
<td>9.3</td>
<td>8.1</td>
<td>1.035–1.084</td>
</tr>
<tr>
<td>SDNR</td>
<td>1.07</td>
<td>79.0</td>
<td>26.0</td>
<td>1.06–1.20</td>
</tr>
<tr>
<td>SNR</td>
<td>1.04</td>
<td>33.0</td>
<td>34.0</td>
<td>1.08–1.20</td>
</tr>
</tbody>
</table>

(b) Stoichiometric values

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>9</th>
<th>15</th>
<th>20°C or above</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Rainy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD loads (kg/d)</td>
<td>9.6</td>
<td>18.1</td>
<td>22.5</td>
<td>4.26</td>
</tr>
<tr>
<td>N</td>
<td>1.39</td>
<td>2.5</td>
<td>3.01</td>
<td>1.25</td>
</tr>
<tr>
<td>P</td>
<td>0.19</td>
<td>0.29</td>
<td>0.35</td>
<td>0.11</td>
</tr>
<tr>
<td>PHACOD storage/P released</td>
<td>1.1</td>
<td>2.3</td>
<td>1.8</td>
<td>–</td>
</tr>
<tr>
<td>COD consumed/P released</td>
<td>7.3</td>
<td>4.1</td>
<td>6.5</td>
<td>3.4</td>
</tr>
<tr>
<td>PHA consumed/P uptake</td>
<td>0.22</td>
<td>0.65</td>
<td>0.6</td>
<td>–</td>
</tr>
</tbody>
</table>

**Figure 5** Comparison of measured and computed COD consumed for NOx-N removed

**Biomass composition**

Figure 6 shows the measured intracellular matter (IM) including Px and PHA, and EPS contents at the end of the aerobic stage after 250 days during the operating period. The IM expressed as % of the sludge produced generally was decreased as temperature increased. However it should be remembered that the organic loads were increased along with temperature increase, and the sludge production was accordingly increased as temperature increased.

The % Px and PHA decreased as the temperature increased. This suggests the PAO took more part in the total microbial mass; in other words, the PAO was more active. However, the removal efficiency was lower at lower temperatures, because the substrate was limited. Figure 6 also supports this statement, since it shows the estimated Px from the mass balance also presents the same trend. The EPSp (EPS protein) seemed not to vary with temperature, while EPSc (EPS carbohydrate) seemed to vary significantly with temperature unlike the result from Atkinson (1991).
Summary and conclusions
The proposed BNR configuration used for this study seemed to reduce the effects of temperature and low load, since more than 70% of NH₄-N and P removal were achieved at temperatures below 10°C. The COD load was greatly reduced at about 60%, while the nutrient loads were reduced to 20 to 30% of the average loads during the rainy period. The study results from more than 400 days operation brought the following conclusions.

The SDNR was mostly significantly affected by temperature. The other kinetic rates showed less effect. The substrate level also affected SPRR and SDNR. This suggests that denitrification is one of the most important parameters to be considered in this BNR configuration.

PHA stored for P release varied from 1.1 to 2.3, and PHA consumed for P uptake varied from 0.22 to 0.65 g COD/g P. The computed values of COD removed for NOₓ-N removed were different from those measured values suggesting the heterotrophic yield might not be constant.

Intracellular matter contents like % Px and PHA were decreased as the temperature increased. This suggests the phosphorus accumulating organisms were in favor of low temperature. However, the lower phosphorus removal was probably due to the low COD and P loads during the low temperature period.

Acknowledgements
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References

Figure 6: Biomass contents of aerobic stage along with temperature


