The performance of a nitrogen-fixing SBR

M.A. Dennis, M.L. Cotter, A.H. Slade and D.J. Gapes

Forest Research, Private Bag 3020 Rotorua, New Zealand
(E-mail: marie.dennis@forestresearch.co.nz; daniel.gapes@forestresearch.co.nz)

Abstract A laboratory study has successfully demonstrated that a nitrogen deficient thermomechanical pulping wastewater can be effectively treated in a sequencing batch reactor (SBR) operated under conditions of biological nitrogen fixation (the N-ViroTech® process). In comparison to continuous stirred tank reactor activated sludge (CSTR-AS) configurations operated under either nitrogen fixing or nitrogen supplemented conditions, slightly lower removals of dissolved organic material were observed in the SBR. However, this was largely offset by significantly better suspended solids removal in the SBR, which contributes to the overall COD discharge. The settleability and dewaterability of sludge produced by the SBR was significantly better than that obtained from the nitrogen fixing CSTR-AS reactors, and comparable to that of a nitrogen supplemented system. Consistently low total and dissolved nitrogen discharges from the N-ViroTech® systems demonstrated the advantage of this system over ones requiring nitrogen supplementation. The feast–famine regime of an SBR-type configuration has significant potential for the application of this technology in the treatment of nitrogen deficient waste streams, particularly those in which conventional single-stage systems may be susceptible to sludge bulking problems.

Keywords Bulking; CSTR; dewatering; floc structure; nitrogen fixation; pulp and paper; SBR; settling

Introduction

For wastewaters that are deficient in nitrogen and/or phosphorus, historical practice has dictated that they cannot be effectively treated using microbiological processes without the addition of supplementary nutrients, such as urea and phosphoric acid. Supplementation is a difficult step to manage efficiently, requiring extensive post-treatment monitoring and some degree of overdosing to ensure sufficient nutrient supply under all conditions. As a result, treated wastewaters may contain excess amounts of both nutrients, leading to impacts such as eutrophication on the receiving waters.

N-ViroTech® is a process which relies on the oxidation of carbonaceous organic pollutants by communities of nitrogen-fixing bacteria. These organisms are able to directly fix nitrogen from the atmosphere, thus satisfying their cellular nitrogen requirements, while maintaining extremely low nitrogen discharges in the final effluent.

Significant advantages over conventional treatment technologies have been identified, including:

• Elimination of nitrogen supplementation, thus achieving significant cost savings;
• Self-regulation of nitrogen requirements, as the bacteria only use as much nitrogen as they require, allowing for substantially less operator intervention and monitoring;
• Improved environmental performance. Nutrient loadings in the final treated effluent for selected nitrogen species may be greatly reduced when compared to conventional systems.

Nitrogen fixation in wastewater treatment has been a major research focus at Forest Research over the past 10 years. Many aspects of N-ViroTech® operation have been explored at laboratory-, pilot- and full-scale to develop a fundamental understanding of key process control parameters (Bruce and Clark, 1994; Clark et al., 1997; Gapes et al., 1999; Slade et al., 2001, 2003, 2004; Reid et al., 2002a, b). Sludge quality, with respect to solids settleability and sludge dewaterability, is a key component of full-scale implementation of
any activated sludge technology. Treatment of pulp and paper wastewaters is known to be susceptible to sludge bulking problems, particularly under fully mixed operation (Thompson and Forster, 2003; Andreasen et al., 1999). Manipulation of system configuration to provide a feast–famine regime may offer an opportunity for significant sludge quality improvement (Andreasen et al., 1999) and trials to assess the performance of SBR N-ViroTech® operation have been initiated. Operating solids retention time has also been implicated in sludge quality improvements, and optimisation of this control parameter is required. A recent full-scale trial of the technology has highlighted the need for a more in-depth understanding of the factors controlling solids settleability in a nitrogen-fixing activated sludge system.

This paper therefore presents the laboratory-scale performance and operation of the N-ViroTech® process under SBR configuration at two solids retention times. The work comprises part of a wider study optimising the N-ViroTech® process for wastewaters susceptible to sludge bulking problems. Conventional nitrogen supplemented operation has been included as a benchmark.

**Methodology**

The study was undertaken using identical 5L laboratory reactors, treating wastewater sourced from a New Zealand mill producing around 1,000 dry tonne.d⁻¹ of thermomechanical pulp (TMP). The wastewater resulted from the pulping of *Pinus radiata*, and was made up from several sources, including thermomechanical pulping wastewater (TMP), refiner mechanical pulping wastewater (RMP), stone groundwood pulping wastewater (SGW) and some paper machine whitewater.

Nitrogen fixing reactors were operated in either continuous stirred tank activated sludge (CSTR-AS) or SBR configuration. Two reactors within each configuration were operated at a nominal solids retention time of 5 and 10 days based on wastage rate. Due to solids carryover in the effluent, the actual SRT was shorter (Table 1). Details of the various configurations are provided in Table 1, along with a summary of the important operating conditions.

As discussed above, the work described herein comprises part of a larger study on the performance of the N-ViroTech® process. For the part of the study described, the feed was diluted with 1 part distilled water in 2 parts effluent.

The seed for each of the reactors was obtained from laboratory systems that had been operated successfully for previous experimental studies, also fed on TMP wastewater. The reactors were fed TMP effluent diluted 1:2 (effluent:water) for 19 days, after which the feed concentration described in the current work was applied. The reactors were then allowed to

| Table 1 | Operating conditions of laboratory reactors |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|              | NFIX-SBR1 SBR  | NFIX-SBR2 SBR  | NFIX-C1 CSTR-AS | NFIX-C2 CSTR-AS |
| Volume        | 4.2            | 4.2            | 4.9            | 4.9            |
| HRT (d)       | 1.3            | 1.4            | 1.7            | 1.5            |
| SRT (d)       | 3.6            | 6.0            | 3.5            | 6.5            |
| Dissolved oxygen (DO) setpoint (mg.L⁻¹) | 0.35 | 0.35 | 0.35 | 0.35 |
| Temperature (°C) | 35             | 35             | 35             | 35             |
| Organic load: |                |                |                |                |
| kgCODₙ.m⁻³.d⁻¹ | 1.43 (0.15)    | 1.31 (0.13)    | 1.09 (0.13)    | 1.22 (0.077)   |
| kgCODₚ.m⁻³.d⁻¹ | 1.06 (0.12)    | 0.97 (0.11)    | 0.81 (0.10)    | 0.903 (0.062)  |
| kgBOD₅.m⁻³.d⁻¹ | 0.643 (0.072)  | 0.607 (0.052)  | 0.509 (0.045)  | 0.561 (0.022)  |

Downloaded from https://iwaponline.com/wst/article-pdf/50/10/269/419342/269.pdf by guest
approach steady state with respect to key performance data (COD, suspended solids, settleability), which was attained after 20 days.

Phosphorus was added to all the systems to provide 5 mg.L\(^{-1}\) PO\(_4\)-P, by adding a stock solution of sodium dihydrogen orthophosphate to give a COD:P ratio of 100:0.25 (mass basis).

The nitrogen fixing systems require excellent dissolved oxygen control. This parameter was controlled via a programmable logic controller (PLC) using proportional/integral/derivative (PID) feedback from the DO sensor, controlling variable output 0-2 L/min air pumps (ASF Thomas, 12V, Model 50020408, Germany). Temperature was controlled by passing hot or cold water through the water jackets.

The SBR reactors were run on a 6 h cycle, with the various phases being: anoxic feed (0.5 h); aerobic react (4.75 h); settle (0.5 h); decant (0.0833 h); waste (0.0833 h); finish buffer time (0.08333 h, used to maintain computer program robustness). To maintain the appropriate SRT, sludge was wasted from the mixed contents obtained after effluent decanting.

The external clarifier on the CSTR-AS reactors had a working volume of 900 ml. The recycle ratio for these systems was maintained at 1 and sludge was wasted from the mixed liquor.

In order to benchmark the performance of the N-ViroTech® systems, two reactors with CSTR-AS configuration were operated with supplemental nitrogen addition (added in the form of urea). The operating COD:N:P ratio of the feed to these supplemental reactors (labelled Nsupp-C1 and -C2) was 100:1.6:0.4 (mass basis), while the reactor DO setpoint was 2.1 mg.L\(^{-1}\). The higher DO was maintained to reflect the benchmarking status of these reactors, given that conventional treatment systems operated for carbon removal utilise DO setpoints of greater than 1 mg.L\(^{-1}\). Otherwise all operational parameters were the same as for the NFIX-CSTR reactors.

**Analytical methods**

Total and volatile suspended solids were performed according to APHA *Standard Methods* 2540 D (APHA, 1998). Dissolved organic carbon was measured on a filtered sample using a Shimadzu Model TOC5000 analyser and the manufacturer’s recommendations. The instrument fulfils the requirements of *Standard Methods* 5310B (APHA, 1998). Carbonaceous BOD\(_5\) was determined according to *Method* 5210B (APHA, 1998). COD was determined using a micro-scale adaptation of *Method* 5220D (APHA, 1998). SVI was determined using a method similar to *Method* 2710D (APHA, 1998) without stirring of the sample and using smaller volumes due to restrictions on the amount of sample available. Nitrogen and phosphorus species were determined according to *Method* 4500 (APHA, 1998).

Capillary suction time (CST), which measures the rate of drainage of a liquid sample through a standard filter paper via capillary action, was determined according to *Method* 2710G (APHA, 1998). This analysis provided a repeatable measure with which to compare the dewaterability of different sludges.

**Detection of nitrogen fixation activity**

Atmospheric dinitrogen (N\(_2\)) is reduced to ammonium within nitrogen fixing organisms, with the help of the nitrogenase enzyme. An assay commonly used to detect the presence of nitrogen fixation is the acetylene reduction assay (Sprent and Sprent, 1990), as, in the presence of nitrogenase, acetylene is preferentially reduced to ethylene (ethene).

For the acetylene reduction assay, a 5 mL mixed liquor sample was pipetted into a 30 ml vial. The samples were sparged with argon for approximately 60 s then capped with a
rubber septum. Acetylene (produced by reacting tap water with calcium carbide in a 1 L conical flask and captured into a rubber bladder) was added (0.6 mL) to the headspace of the vial, after an equal volume of headspace had been withdrawn. The samples were then shaken in a 35°C waterbath for 30 min. 5-10 mL headspace was removed from each sample, and this was injected into a gas chromatograph (1.5 m, ¼” i.d. column containing Porapak N, 80/100 mesh). An ethylene peak 10× greater than that of the blank was taken as indicative of nitrogenase activity.

Results and discussion
The characteristics of the reactor feed are described in Table 2. The TMP effluent had a relatively high COD, most of which was soluble. Slightly acidic, it had significant levels of colloidal material, evidenced by the turbid nature of the material passing through glass fibre filter paper (Whatman GFC, England). The unsupplemented feed was deficient in both nitrogen and potentially phosphorus, by generally accepted standards (COD:N:P of 100:0.34:0.25).

Confirmation of nitrogen fixation
The acetylene reduction assay was conducted to determine the presence of nitrogen fixing activity. As expected, the only reactors to yield a positive response to the assay were those operating under N-ViroTech® conditions.

Nitrogen supplemented benchmark
The performance of the reactors operated with supplemental nitrogen addition is summarised in Table 3. For comparison, the performance of the Nitrogen fixing CSTR systems are also presented.

The COD₃, DOC and BOD₅ parameters shown in the Table 3 demonstrate that the N-ViroTech® process, operating in CSTR-AS configuration, was able to treat the TMP wastewater in essentially the same fashion as a conventional nitrogen supplemented system.

The recorded SVIs for all of the reactors are relatively high, which demonstrates the propensity for this TMP wastewater to produce a bulking sludge. Under the higher SRT condition, the Nsupp reactors produced a significantly better SVI than the NFIX reactor, reflected in the better effluent VSS and CODt values.

The recorded CST values were high for the nitrogen fixing system, indicative of a sludge that may be difficult to dewater.

Table 2 Feed characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Average (95% confidence interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical oxygen demand, total</td>
<td>COD₄</td>
<td>1,864 (91)</td>
</tr>
<tr>
<td>Chemical oxygen demand, soluble</td>
<td>COD₃</td>
<td>1,377 (83)</td>
</tr>
<tr>
<td>Biochemical oxygen demand</td>
<td>BOD₅</td>
<td>819 (48)</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
<td>DOC</td>
<td>495 (16)</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>TSS</td>
<td>178 (30)</td>
</tr>
<tr>
<td>Volatile suspended solids</td>
<td>VSS</td>
<td>174 (29)</td>
</tr>
<tr>
<td>Total Kjeldahl nitrogen</td>
<td>TKN</td>
<td>6.3 (2.4)</td>
</tr>
<tr>
<td>Dissolved Kjeldahl nitrogen</td>
<td>DKN</td>
<td>1.9 (1.2)</td>
</tr>
<tr>
<td>Ammoniacal nitrogen</td>
<td>NH₄⁺-N</td>
<td>0.1 (0.0)</td>
</tr>
<tr>
<td>Total oxidised nitrogen</td>
<td>NO₃⁻</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>TP</td>
<td>4.6 (1.6)</td>
</tr>
<tr>
<td>Dissolved reactive phosphorus</td>
<td>DRP</td>
<td>3.8 (1.6)</td>
</tr>
<tr>
<td>COD:N:P</td>
<td>mg:mg:mg</td>
<td>100:0.34:0.25</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>4.5 (0.1)</td>
</tr>
</tbody>
</table>
The extremely low effluent nitrogen data in Table 3 clearly demonstrates the advantage of the N-ViroTech® process. Conversely, the nitrogen discharges from the benchmarking reactors were significantly higher, reflecting the difficulty in managing nutrient supplementation to a nitrogen-deficient wastewater.

### Treatment performance of nitrogen fixing reactors

The reactors’ performance (as determined by the mixed liquor VSS and the effluent parameters COD, VSS) over the experimental time period is highlighted in Figures 1–4, while average removals for various parameters are summarised in Figure 5.

The mixed liquor suspended solids was fairly constant in most of the reactors, with only the NFIX-SBR2 showing a notable decrease in concentration during the first 5–7 days of the experiment (Figure 1). The reactors operated at comparable SRTs had similar biomass concentrations, and those with longer SRT maintained higher biomass concentrations.

The removal of soluble organic material, as measured by COD₅ and DOC, appears consistently lower for the SBR systems (Figures 2 and 5). It is clear that increased SRT resulted in greater removal of these soluble components, for both reactor configurations. At the higher SRTs, acceptable removals of greater than 70% were obtained. The BOD₅ was reduced by 80–95% in all systems, with no significant differences between reactors.

The effluent COD, and VSS performance data is depicted in Figures 3–5. The VSS from NFIX-C1 was observed to improve throughout the first half of the trial (Figure 4), which does impact the averages reported for this (and also the COD, parameter). However, the figures do show that the SBR configuration clearly outperformed the CSTR-AS over the
trial period, with VSS discharges consistently less than 100 mg.L⁻¹ (Figure 4). In contrast, the CSTR-AS displayed poor solids removal. Reflecting this lower discharge of solids, there is essentially no significant difference in CODₜ removals when comparing the reactors operated at similar SRTs.

The average nutrient discharges are presented in Figure 6. For these reactors, the dissolved nitrogen species were consistently very low, with the ammonium and NOₓ species below detection levels. There were no significant differences attributable to SRT or between the two N-ViroTech® reactor configurations.

**Sludge quality**

The sludge quality was assessed using the SVI and CST parameters. Figure 7a indicates poor settleability for the majority of reactors, with average SVIs less than 200 mL·g⁻¹ only observed for NFIX-SBR1. Inspection of Figure 7b provides a better insight into the settleability performance. Much of the data variation occurred within the first two weeks of the experimental period, with much more consistent SVIs for the latter period. For this period, only the SVIs for the CSTR stand out as indicative of a bulking sludge.
The SVI results suggest that the SBR configuration did outperform the CSTR-AS with respect to sludge settleability. This is clearly reflected in the suspended solids removals discussed above (Figure 5).

Unlike the SVI results, those obtained for CST were quite clear. The SBR system produced a biomass with significantly better dewaterability than the nitrogen fixing CSTR-AS. Given that the CST experiments ceased after 100 s, the dewaterability for these latter reactors could only be concluded to be poor.

These results demonstrate that operation under SBR configuration did result in a better quality activated sludge for the nitrogen fixing system.

The floc structure from the various reactors is revealed in Figure 8. The SBR system had significantly greater floc size than in the other reactors, and displayed a floc density greater than those from the nitrogen fixing CSTR-AS. Virtually no filaments protruded from the floc structures in the SBR systems, whereas NFIX-C2 did display a high filamentous abundance. The flocs obtained from the benchmarking reactors appeared to have good density, were smaller than those from the SBR system, and displayed some evidence of filamentous protrusion from the floc structure.
This microscopic evidence is consistent with the SVI and CST results. The high SVIs obtained in the nitrogen fixing CSTR-AS could be attributable to bulking due to both filamentous and non-filamentous bulking. The latter can be a result of excessive production of extracellular polymeric substances (EPS), which are capable of holding large amounts of water, thus reducing their density (Peng et al., 2003; Tchobanoglous and Burton, 1991) as is seen in Figure 8 c and d. The high CST for these reactors could be attributable to overproduction of extracellular polymeric material (EPS) within these systems, suggested by the low bacterial density of the flocs produced.

**Implications of results**

Overall, the NFIX-SBR configuration performed well, when compared with the CSTR-AS systems operated either under nitrogen-fixing or conventional (nitrogen-supplemented) conditions. Slightly lower removals of dissolved organic material were offset by improvements in sludge settleability, dewaterability and suspended solids removal.

The sludge quality improvements of the NFIX-SBR over that of the NFIX-CSTR mimics results obtained by other authors. The feast/famine mode of operation of SBR (or plug flow reactors) appears to provide an advantage to floc forming bacteria over filaments (Andreasen et al., 1999), and relatively large floc structures can predominate (Gapes, 2003;
Keller pers comm.). These factors aid in the production of a successfully settling, dewaterable biomass. The advantages of this configuration for application to wastewaters which may be especially susceptible to producing a bulking sludge are therefore evident.

Nutrient deficiency in a treatment system has been linked to the presence of bulking sludge, due to the overproduction of extracellular polymeric substances (Peng et al., 2003; Tchobanoglous and Burton, 1991). Further, certain nitrogen fixing bacteria (e.g. *Azotobacter vinelandii*) are known to produce significant amounts of this material (Berkeley et al., 1979).

A number of approaches to improved sludge control in the N-ViroTech® system are currently being assessed, including the role of system configuration: hence the focus of this paper on SBR systems. The current work has demonstrated that sludge quality need not limit the development of nitrogen fixing activated sludge systems. Overall, it is believed that operation of N-ViroTech® under the feast–famine conditions exhibited in SBR systems has lead to a significant improvement of the technology.

Conclusions
This laboratory study has successfully demonstrated that a nitrogen-deficient thermomechanical pulping wastewater can be effectively treated in an SBR operated under conditions of biological nitrogen fixation (the N-ViroTech® process). The following findings were obtained from the study:

- Slightly lower removals of dissolved organic material in the SBR, relative to continuous stirred tank activated sludge (CSTR-AS) configurations operated under either nitrogen fixing or conventional, nitrogen supplemented conditions. However, this was largely offset by significantly better suspended solids removal in the SBR, which contributes to the overall COD discharge. Biochemical oxygen demand (BOD₅) removals were high and comparable in all configurations assessed.
- The settleability and dewaterability of sludge produced by the SBR was significantly better than that obtained from the nitrogen fixing CSTR-AS reactors, and comparable to that of a nitrogen supplemented system.
- Consistently low total and dissolved nitrogen discharges from the N-ViroTech® systems demonstrated the advantage of this system over ones requiring nitrogen supplementation.

In conclusion, the feast–famine regime of an SBR-type configuration has significant potential for the application of this technology in the treatment of nitrogen deficient waste streams, particularly those in which conventional single stage systems may be susceptible to sludge bulking problems.

References


Keller, J. (pers. comm.) University of Queensland, Australia.


