Balancing yield, kinetics and cost for three external carbon sources used for suspended growth post-denitrification

Y. Mokhayeri, R. Riffat, S. Murthy, W. Bailey, I. Takacs and C. Bott

ABSTRACT

Facilities across North America are designing plants to meet stringent limit of technology (LOT) treatment for nitrogen removal. In the Mid-Atlantic region of the United States, this is in response to the Chesapeake Bay Agreement, which limit effluent total nitrogen discharges from wastewater treatment plants to between 3–5 mg/L. Since denitrification is crucial for the removal of nitrogen, maximizing this process step will result in a decrease in nutrient load to the receiving waters. Of particular interest is the use of an alternate external carbon source to replace the most commonly used carbon, methanol. Three external carbon sources were evaluated in this study including: methanol, ethanol and acetate at 13°C. The aim of this study was to evaluate the relative benefits and constraints for using these three carbon types. Laboratory scale Sequencing Batch Reactors (SBRs) were set up to grow and acclimate carbon free biomass to the specified substrate while in-situ Specific Denitrification Rates (SDNRs) were conducted concurrently. The results suggest that the SDNRs for acetate (31.0 ± 4.6 mgNO_3-N/gVSS/hr) and ethanol (29.6 ± 5.6 mgNO_3-N/gVSS/hr) are higher than that for methanol (10.1 ± 2.5 mgNO_3-N/gVSS/hr). The yield coefficients in g COD/g COD were observed to follow a similar trend with values of 0.45 ± 0.05 for methanol, 0.53 ± 0.06 for ethanol and 0.66 ± 0.06 for acetate.

Key words | acetate, denitrification, ethanol, methanol, sequencing batch reactor, yield

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INTRODUCTION

Wastewater treatment plants in the Chesapeake Bay region are interested in improving performance of their existing denitrification processes. This is in response to the Chesapeake Bay Agreement, which will limit effluent total nitrogen to between 3–5 mg/L. An important step for nitrogen elimination in wastewater treatment is heterotrophic denitrification. In this process, organic substrates are utilized as electron donors by denitrifying bacteria, and the electron acceptor (nitrate and/or nitrite) in the anoxic reactor is converted to nitrogen gas.

When essentially complete nitrogen removal is required, an external source of carbon containing no nitrogen will be used. External carbon addition typically is needed to attain low effluent nitrate concentrations because of carbon limitations/availability in the wastewater. Blue Plains Advanced Wastewater Treatment Plant (AWTP) in Washington, DC is the largest point source wastewater treatment plant discharging into the Potomac River that makes its many to the Chesapeake Bay. The plant is one of the many wastewater treatment plants evaluating its ability to meet future discharge limits and is specifically interested in assessing the use of external sources of organic carbon. The plant currently uses methanol as an external carbon source in a post denitrification process. Methanol is commonly used for denitrification because of its low cost and ability to denitrify without leaving a residual

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biochemical oxygen demand (BOD) in the process effluent. The process achieves low total nitrogen values in summer, while during winter (January, February and March) the process is more difficult to operate due to a decline in microbial growth rates. One approach to improve this limitation is to utilize an alternate substrate for denitrification in place of methanol during the winter, promoting the growth of organisms and thus increasing the rate of denitrification. Different external carbon sources such as methanol, ethanol, glucose and acetate have been successfully used to enhance denitrification process (Her & Huang 1995 and Zhao *et al.* 1999). However, it has been suggested that a complete evaluation of different carbon sources for denitrification is largely missing.

The denitrification potential of wastewater is primarily determined as the stoichiometric ratio between the organic compound used and the nitrate, which is usually expressed as the COD/N or the BOD/N ratio. Some COD/N ratios reported for methanol are 4.45 g COD/g NO_3-N in the continuous experiments; and 4.0 at 15°C and 4.16 g COD/g NO_3-N at 25°C in pure culture batch cultivations (Christensson *et al.* 1994). Mycielski *et al.* (1983) reported a requirement of 2.0 g ethanol to denitrify 1 g of NO_3-N, corresponding to a COD/NO_3-N ratio of 4.16. Generally, heterotrophic denitrification processes with acetic acid as a carbon source need a COD/NO_3-N ratio of 3.1 to 3.7 for the denitrification (Kim & Son 2000).

Yield is an important parameter in the selection of alternate substrates. Grady & Lim (1981) observed yield for methanol between 0.57 and 0.66. Timmermans & Haute (1983) observed a yield value of about 0.4 at a pH of 7.0. Dold *et al.* (2008) estimated the yield coefficient of 0.4 mg COD/\mg COD for the methanol-utilizing heterotrophs.

Using methanol as the external carbon source, values of maximum specific growth rate ranging from 0.2 to 2.0 d^{-1} were reported by Gaudy & Gaudy (1980). In earlier studies, Stensel *et al.* (1973) reported maximum specific growth rates of 0.52 and 1.86 d^{-1} at 10°C and 20°C, respectively. Dold *et al.* (2008) reported the maximum specific growth rate of methanol-utilizing organisms at approximately 1.3 d^{-1} at 20°C. Mokhayeri *et al.* (2006) observed a higher maximum specific growth rate of 4.0 d^{-1} at 20°C for organisms utilizing acetate or sugar for denitrification. Christensson *et al.* (1994) reported the maximum specific growth rate for methanol at 15°C and 25°C as 0.8 and 2.1 d^{-1}, respectively. They reported values of 1.9 and 4.8 d^{-1} when using ethanol as a carbon source, suggesting a higher growth rate with ethanol compared to methanol. Table 1 provides the comparative costs of the three substrates.

Table 1 | Comparative costs for three substrates (Katehis 2007)

Carbon source	$/kg	$/kg-COD
Methanol	0.33	0.22
Ethanol	0.84	0.40
Acetate	1.03	0.97

The overall objective of this research was to evaluate three external sources of carbon–methanol, ethanol and acetate in terms of yield, SRT (Solids Retention Time) and denitrification rates at cold temperature.

METHODS

Batch reactor set-up

Three laboratory-scale SBRs were employed in the study, each with a different carbon substrate–methanol, ethanol or acetate (Figure 1). The units were seeded with sludge from Piscataway wastewater treatment plant (Accokeek, Maryland, USA). The plant is a step feed biological nutrient removal (BNR) system that did not use any external carbon.

Each SBR was operated inside a temperature-controlled incubator at 13°C. The reactors were operated at a cycle time of 6 hours. Each cycle consisted of influent feeding, aerobic reaction, oxygen stripping, carbon feeding, anoxic reaction, re-aeration, waste discharge, sludge settling, effluent decanting and idling. Each SBR cycle commenced with influent feeding consisted of tap water spiked with 40 mg/L NO_3-N, 6 mg/L NH_3-N and 5 mg/L PO_4-P. In addition, 1.78 mg/L of $Na_2(SO_3)$ was also added to the feed to dechlorinate the tap water. Feeding was followed by a 2.25 hour aerated period. Aeration was provided by house compressed air through an aquarium-style diffuser stone. Aeration was then stopped and a 0.25 hour period ensured that dissolved oxygen (DO) decreased to zero before adding the carbon substrate. Carbon was added during the first 2 minutes of the anoxic phase at 38.4 ml/day. Each reactor was fed with a different substrate, e.g. methanol, ethanol or acetate. During anoxic phase, nitrogen gas was used to

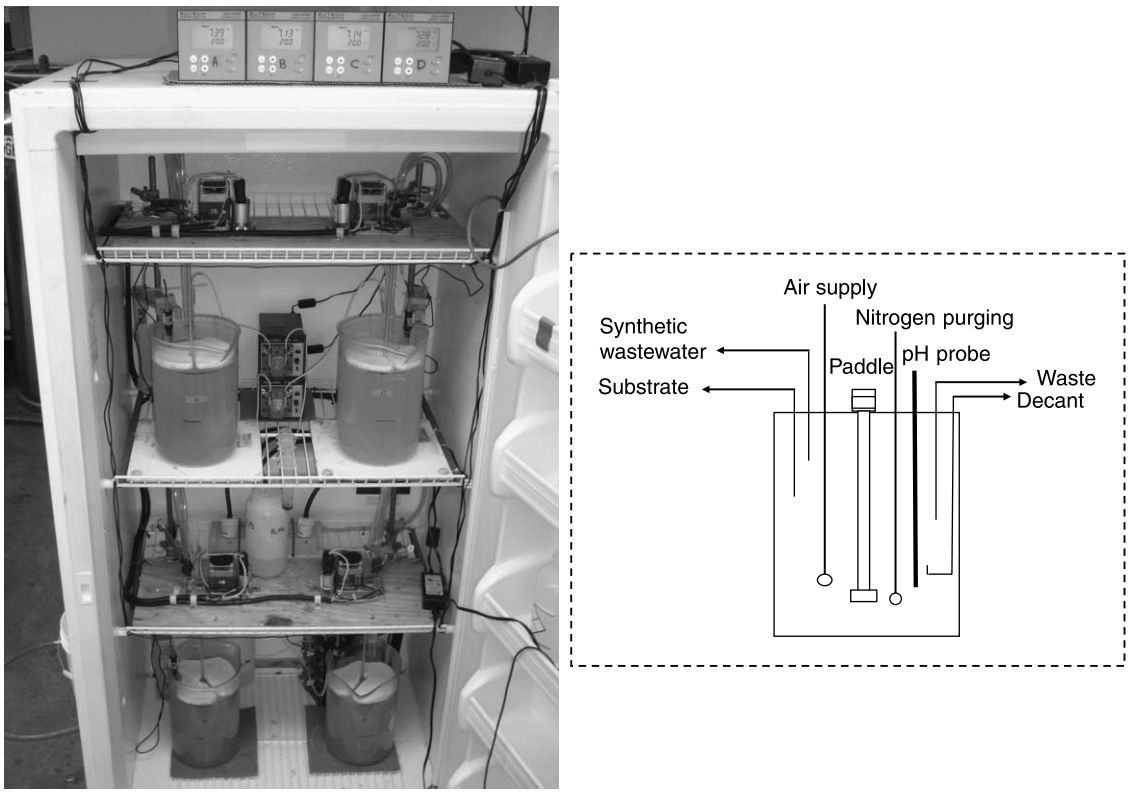

Figure 1 | Laboratory scale SBRs.

maintain anoxic condition and a floating Styrofoam lid was also used as a barrier for oxygen transfer into the liquid. During this cycle, pH controllers were used to keep the pH at 7.5 ± 0.1 by adding sulphuric acid. During the anoxic cycle typical changes in pH varied between 7.40 and 7.63, and ranged between 7.0–7.1 in the aerobic cycle. The reactors employed in this study are illustrated in Figure 1.

After a further 2-hour anoxic period, the SBRs were aerated for 0.25 hours before settling and decanting. After the settling period, 1.75 L of supernatant was removed, resulting in a hydraulic retention time (HRT) of 12 hours. The reactors were continuously mixed with a mechanical mixer, except during settling and decanting periods. The operating mode was selected to imitate the exposure of denitrifying biomass to alternating aerobic-anoxic conditions encountered in practice at the Blue Plains AWTP.

Analyses

Monitored parameters included pH, DO, temperature, nitrate, nitrite, chemical oxygen demand (COD), mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS). All parameters were measured according to Standard Methods (1998). Soluble nitrate, nitrite and COD were tested using a Hach DR4000 Spectrophotometer. All analyses were conducted at Blue Plains AWTP laboratory in Washington DC.

SDNR test

It is important to observe the rate at which biomass acclimates to the carbon source. From the second day of operation, until steady state was achieved, SDNR tests were performed at intervals of a few days. These SDNR values were calculated from the slope of the nitrate profile after substrate addition. The SDNR (mg NO_3-N/g VSS/hr) was obtained by collecting 6 samples during the anoxic period prior to the depletion of COD or NO_3-N. Samples were collected with a syringe and filtered immediately with 0.45 μm syringe filters. Analysis commenced immediately after sampling.

Figure 2 shows an example of the nitrate profile observed in the SBRs during a cycle at 13°C. During

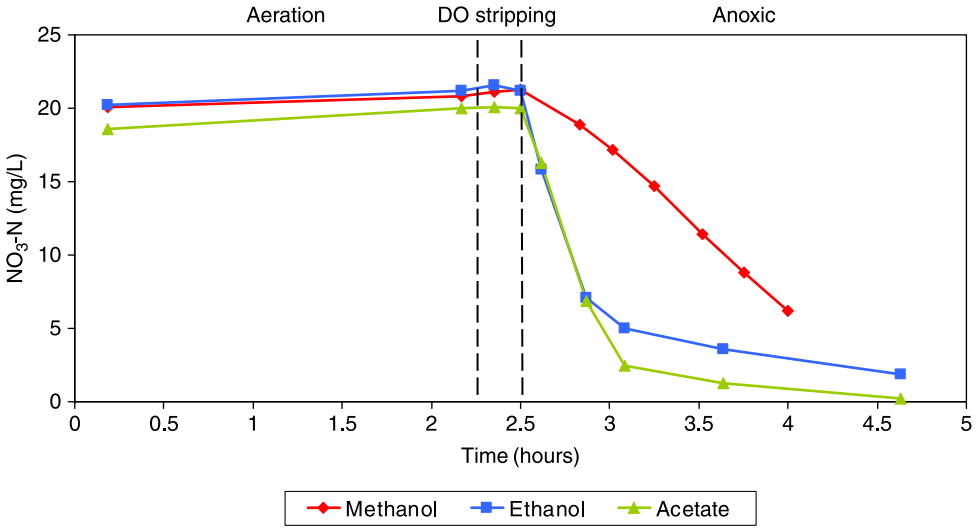

Figure 2 | Example of a typical nitrate profile in an SBR.

the first 2.25 hours (aerated) nitrate concentration remained essentially constant at a level determined by the influent concentration. For 0.25 hours after aeration stopped (DO stripping), there was a small decrease in nitrate due to endogenous denitrification. After the carbon substrate was added at 2.5 hours, the nitrate showed a steady decrease over the remainder of the unaerated phase.

The SDNR is reported with units of mg NO_3-N/g VSS/hour as per Equation (1).

$$\text{SDNR}\,(\text{mg}\,NO_3\text{-N/g}\,\text{VSS/hour}) = \frac{\text{Slope of}\,NO_3\text{-N response curve}}{\text{VSS}} \quad (1)$$

where, VSS = Volatile Suspended Solids concentration in SDNR test (g/L).

Yield coefficient

It has been proposed that denitrification is a four step process: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

The simplification here is that there is no release of intermediates (NO, N_2O). Therefore, the first process is representing reduction of nitrate to nitrite ($NO_3^- \rightarrow NO_2^-$) and the second a reduction of nitrite to nitrogen gas ($NO_2^- \rightarrow N_2$). If NO_2^- was produced and the reduction proceeded no further, expected COD to convert NO_3-N to NO_2-N (first process) is estimated, as follows:

$$\frac{\text{g substrate COD consumed}}{\text{g}\,NO_2\text{-N produced}} = \frac{1.14}{1 - Y_d} \quad (2)$$

where,

Y_d = yield coefficient, g COD/g COD
1.14 = O_2 equivalent of NO_2-N produced, g O_2/g NO_2-N (Metcalf & Eddy 2003).

For the second process, the expected COD to convert NO_2-N to N_2 can be calculated, as follows:

$$\frac{\text{g substrate COD consumed}}{\text{g}\,NO_2\text{-N removed}} = \frac{1.71}{1 - Y_d} \quad (3)$$

where, 1.71 = O_2 equivalent of NO_2-N removed, g O_2/g NO_2-N (Metcalf & Eddy 2003).

If NO_3^- is denitrified to N_2 with no accumulation of NO_2, the expected COD is represented by the common Equation:

$$\frac{\text{g substrate COD consumed}}{\text{g}\,NO_3\text{-N removed}} = \frac{2.86}{1 - Y_d} \quad (4)$$

where, 2.86 = O_2 equivalent of NO_3-N removed, g O_2/g NO_3-N (Metcalf & Eddy 2003).

The sum of Equations (2), (3) and (4) results in COD consumed during the denitrification process as follows:

$$\text{(mg/L) COD consumed} = \frac{1.14}{1 - Y_d} \times \text{g NO}_2\text{-N produced} + \frac{1.71}{1 - Y_d} \times \text{g NO}_2\text{-N removed} + \frac{2.86}{1 - Y_d} \times \text{g NO}_3\text{-N removed} \quad (5)$$

The yield value is estimated by re-arranging Equation (5).

$$Y_d = 1 - (1.14 \times \text{g NO}_2\text{-N produced} + 1.71 \times \text{g NO}_2\text{-N removed} + 2.86 \times \text{g NO}_3\text{-N removed})/\text{(mg/L) COD consumed} \quad (6)$$

Using the observed COD, NO_3-N, and NO_2-N data collected during the anoxic portion of the cycle, the anoxic growth yield can be estimated and then used to calculate an actual COD/N ratio using Equations (2), (3) and (4).

RESULTS AND DISCUSSION

Activated sludge processes using conventional clarifiers are typically limited by the operating MLSS. Therefore, rather than operating the three SBRs at the same SRT, they were operated at the same hydraulic retention time to produce equivalent MLSS concentrations. The biomass concentrations are provided in Table 2. To achieve equivalent MLSS concentrations, the methanol SBR was operated at a higher anoxic SRT of 12 d compared to the 7 d anoxic SRT of the ethanol and acetate reactors. The reason for this is explained by the following. The MLSS concentration is influenced by the yield. The yield coefficients for the three substrates are presented in Table 3. The yield for ethanol was 17.8% higher compared to that for methanol, while the yield for acetate was 46.7% higher compared to that for methanol. Thus at the same MLSS concentrations, the reactor using methanol can be operated at a higher SRT than the reactors using ethanol and acetate. This SRT bonus is important for the reactor using methanol grown biomass. The maximum specific growth rate of methanol was previously observed to be less than half the growth rate of acetate (Mokhayeri *et al.* 2008). While operating at a higher SRT can improve the ability of the process to denitrify (a process washout would be likely for a 7-day operating SRT for methanol grown biomass), a higher operating SRT for equivalent MLSS concentration would also result in the accumulation of endogenous residue. Alternatively, the active fractions are greater for these two other substrates (ethanol and acetate) compared to methanol. Therefore, despite a lower yield for methanol and higher operating SRT, the combination of accumulation of endogenous residue and lower growth rates results in a lower net SDNR, as shown in Table 4. Table 4 provides the average SDNR values for the three substrates at similar equivalent MLSS, but different anoxic SRTs and active fractions. The denitrification rates and SDNRs for ethanol and acetate were almost three times the rates obtained for methanol.

Using the unit costs from Table 1 (Katehis 2007), the costs based on the data and yield coefficients observed in this research were calculated. These are presented in Table 5.

Table 2 | Biomass concentrations and SRT values for the three SBRs

Carbon source	Average MLSS (mg/L)	Average MLVSS (mg/L)	Average SRT (days)
Methanol	1,030	900	12.0
Ethanol	1,050	892	7.0
Acetate	1,029	885	7.0

Table 3 | Yield coefficients for the three substrates

Carbon source	Yield (g COD/g COD)	Percent of (yield)*	NO_3 to N_2 g COD/g NO_3-N	Percent of (SRT)*
Methanol	0.45 ± 0.05	–	5.19	–
Ethanol	0.53 ± 0.06	117.8%	6.08	58.3%
Acetate	0.66 ± 0.06	146.7%	8.40	58.3%

*Compared to methanol.

Table 4 | SDNR values for the three substrates

Carbon source	Average SDNR (mg NO_3-N/g VSS/hr)	Percent of (rate)*
Methanol	10.1 ± 2.5	–
Ethanol	29.6 ± 5.6	293.1%
Acetate	31.0 ± 4.6	306.9%

*Compared to methanol.

Table 5 | Operating costs for three substrates

Carbon source	$/kg	Yield (g COD/g COD)	$/kg-$NO_3$-N
Methanol	0.33	0.45	1.14
Ethanol	0.84	0.53	2.43
Acetate	1.03	0.66	8.15

We need to consider a number of factors when selecting an appropriate substrate for denitrification. With ethanol and acetate, higher denitrification rates are obtained. However, this is accompanied by a higher yield for these substrates, which results in much more external carbon needed for denitrification, and higher sludge production. Furthermore, unit costs for ethanol and acetate are much higher compared to methanol. This translates to significantly higher overall operations cost (Table 5), even though the initial capital costs may be lower. A balance may be obtained together with effective denitrification at cold temperature, by switching to a substrate such as ethanol only in the winter, while using methanol the rest of the year. A previous study by Mokhayeri *et al.* (2008) indicated that methanol grown biomass could utilize ethanol as a carbon source and ethanol grown biomass could use methanol. Further studies are being conducted using methanol/ethanol substrate blends to investigate this concept further.

CONCLUSIONS

The SDNRs for acetate (31.0 ± 4.6 mgNO_3-N/gVSS/hr) and ethanol (29.6 ± 5.6 mgNO_3-N/gVSS/hr) were observed to be higher than that for methanol (10.1 ± 2.5 mgNO_3-N/gVSS/hr).

The yield coefficients in g COD/g COD were observed to follow a similar trend with values of 0.45 ± 0.05 for methanol, 0.53 ± 0.06 for ethanol and 0.66 ± 0.06 for acetate.

The study shows that the denitrification rates for methanol grown biomass is a third that of acetate and ethanol grown biomass for similar operating MLSS concentrations. However, the operating cost for ethanol is more than twice that of methanol and for acetate is over seven times that of methanol. Over the long run, for the Blue Plains AWTP, the higher operating costs make the use of the more expensive substrates unviable. The possibility of using optimal methanol/ethanol substrate blends should be investigated to maximize rates while minimizing operating costs.

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